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THE CHEMICAL ANALYSIS OF IRON

BY

A. A. BLAIR

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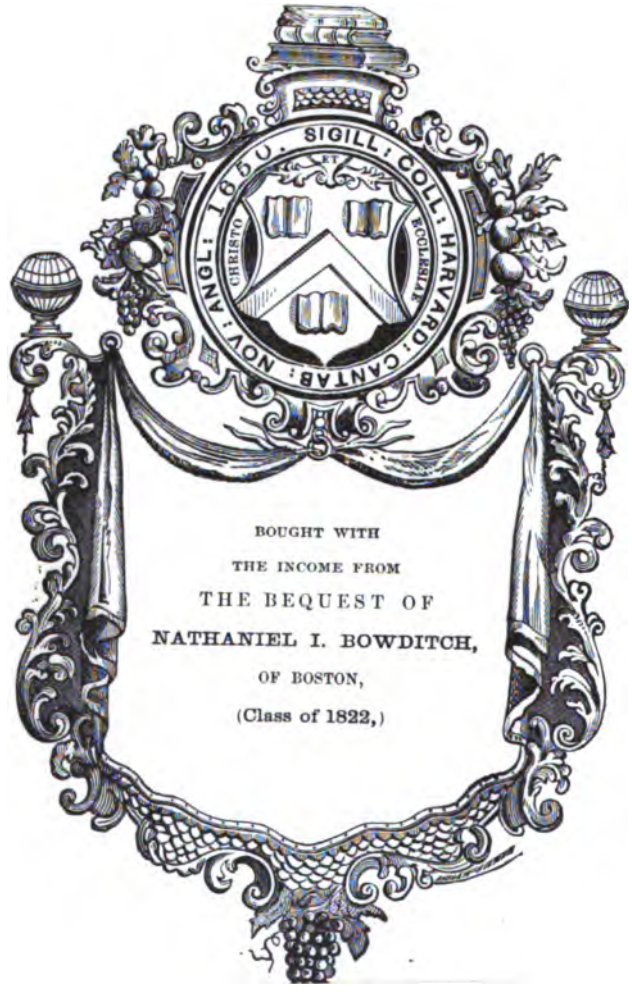

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THE

CHEMICAL ANALYSIS OF IRON

A COMPLETE ACCOUNT OF ALL THE BEST KNOWN METHODS

FOR THE

Analysis of Iron, Steel, Pig-Iron, Alloy Metals, Iron Ore, Limestone, Slag, Clay, Sand, Coal and Coke

BY

ANDREW ALEXANDER BLAIR

GRADUATE UNITED STATES NAVAL ACADEMY, 1866; CHIEF CHEMIST UNITED STATES BOARD APPOINTED TO TEST IRON, STEEL, AND OTHER METALS, 1875; CHIEF CHEMIST UNITED STATES GEOLOGICAL SURVEY AND TENTH CENSUS, 1880; MEMBER AMERICAN PHILOSOPHICAL SOCIETY, ETC.

EIGHTH EDITION

PHILADELPHIA AND LONDON

J. B. LIPPINCOTT COMPANY

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TO

MY WIFE

WITHOUT WHOSE ASSISTANCE IT WOULD NEVER HAVE
BEEN WRITTEN

THIS VOLUME
IS
Dedicated

PREFACE TO THE EIGHTH EDITION.

SINCE the last edition of this book was issued there have been so many improvements in the methods for the determination of the usual elements in iron and steel and the so-called alloy metals have become so important that it was found necessary to recast the work and to rewrite the greater part of it. The various methods employed in the analysis of the alloy steels have been placed together and a separate part has been arranged for the alloy metals. The methods for the analysis of furnace and other gases have been omitted. The table of atomic weights has been corrected to correspond with the values recommended by the Committee for 1918, and the table of factors corrected to correspond with the new values.

PHILADELPHIA, February, 1918.

PREFACE TO THE FIRST EDITION.

THE various methods for the analysis of iron and steel, as well as the descriptions of special apparatus to facilitate the performance of the analytical work, are so widely distributed through transactions of societies, journals, reviews, periodicals, and works on general analytical chemistry that only the possessor of a chemical library can command the literature of the subject. It is my object in the following pages to bring within the compass of a single volume, as nearly as possible, all the methods of real value to the iron analyst, and in doing this to give the credit of originality for the different methods and improvements to the proper persons. In many cases this has been very difficult, and I shall be glad to have any mistake brought to my attention.

This work presupposes some knowledge of general and analytical chemistry, and some practical experience in laboratory work and manipulation, as it is intended to be a guide for the student of iron chemistry only. For such persons the details of the descriptions of the methods will, I hope, often prove of great assistance. With very few exceptions, these descriptions are the results of my own experience in the use of the methods, and the details are those that seemed to me to be of importance in their practical performance. Many of the special forms of apparatus are of my own contrivance; they have proved extremely useful to me, and I hope may facilitate in some cases the work of iron chemists, to whom often very little is given and of whom very much is required.

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THE CHEMICAL ANALYSIS OF IRON.

APPARATUS

THE speed and facility with which results may be obtained, and often the accuracy of these results, are dependent upon various mechanical appliances as well as upon the skill of the analyst. These appliances will be considered under separate heads.

APPARATUS FOR THE PREPARATION OF THE SAMPLES

For crushing iron ores, a mortar and pestle, such as are ordinarily used, have caused much trouble. In breaking up hard ores the wear, especially on the pestle, is considerable, and the particles of cast iron may cause the sample to yield too high a result in the determination of metallic iron. Of course, in non-magnetic ores these particles may be removed with a magnet, but in the case of magnetic or partly magnetic ores this cannot be done, and a hardened steel mortar and pestle should be used. The sample should be broken to about pea size, well mixed, and quartered, this quarter broken still finer, and mixed and quartered in the same way until the resulting portion is small enough to be bottled. The final grinding can be best done on a chilled-iron plate with a hardened steel muller. Except with unusually refractory ores, further grinding is unnecesary, but with such ores the final grinding must be in an agate mortar.

There are many grinding machines for laboratory use which are carried in stock by dealers in Chemical Apparatus, as well as by the various makers of grinding machinery. After the sample has been ground on the chilled plate, it is generally necessary to finish the grinding in an agate mortar. This is usually done by hand, but several methods of

FIG. 1.

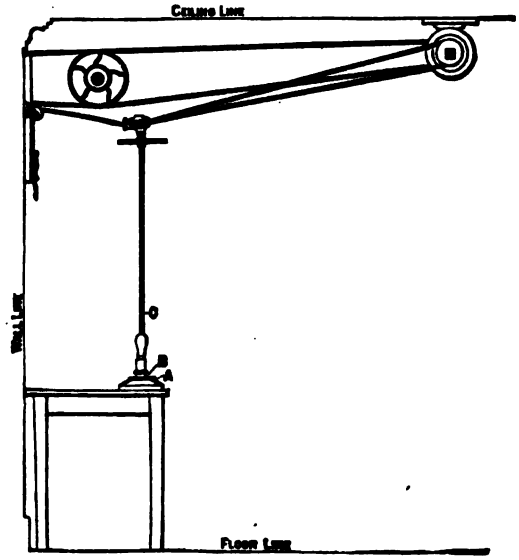
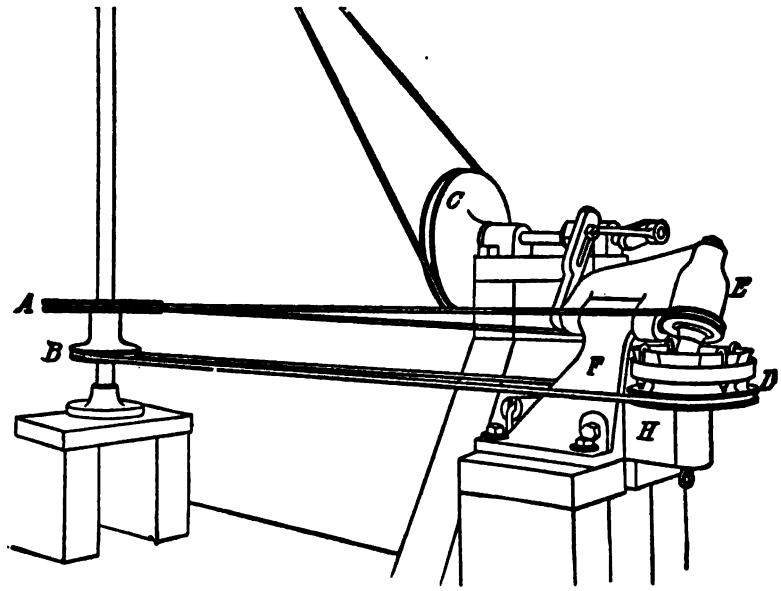


FIG. 2.



applying power have been perfected, the simplest form is shown in Fig. 1, in which the pestle is rotated by a Stow flexible shaft.

The apparatus shown in Fig. 2, designed by Mr. Maunsel White, has been in use several years at the chemical laboratory of the Bethlehem Iron Company, and has worked very satisfactorily. The power is applied from an overhead countershaft not shown in the cut. The lower portion of the vertical shaft carries two horizontal pulleys, A and B; these pulleys are connected, as shown, with the spindle carrying the pestle and with the circular box D, in which the mortar is securely fastened by four claw-bolts, which may be seen in the drawing.

The piece D is made with a spindle which extends down into a bearing in the supporting piece H. The piece H, which may be called a lever, is secured to the frame F by a bolt which passes through it, and around which it can be turned through an angle sufficient to permit of the easy emptying of the mortar without displacing the belt. A groove at the farther end of H, as shown, carries a weighted rod which supplies the pressure of the mortar against the pestle. The weights are made movable so that the pressure can be varied for special cases.

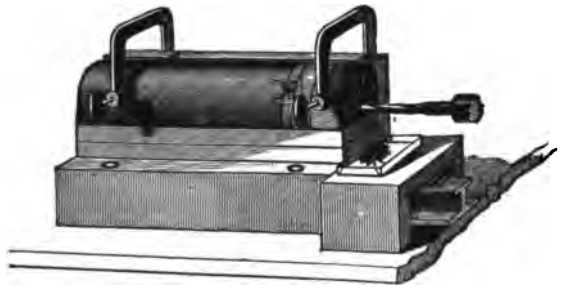
The agate pestle is secured in a brass spindle with a grooved collar for carrying the belt; this spindle revolves in a bored socket in the piece E, and is secured from dropping out by means of a small nut, shown at the top of the piece. The piece E is connected to the frame F by a circular bolt, the end of which is supplied with an arm for rocking the piece E; this obtains by fastening the bolt with dowel-pins where it passes through the piece E while free to move in the frame F. The pulley C is run from the countershaft, and revolves a small shaft whose end carries a crank connected by a short rod to the bolt-arm of the piece E, and supplies the power and means for the rocking motion.

It will now be seen that while the mortar revolves, the pestle, revolving more rapidly, sweeps across the face of the mortar by the rocking motion of the piece E, thus constantly changing the material between the grinding surfaces.

In taking samples of iron or steel, a perfectly clean dry drill should be used, and the utmost care taken to prevent grease, oil, or dirt of any kind from getting in the sample. With bar-iron or steel the scale on the

outside of the piece should be removed as carefully as possible, the first drillings from each hole thrown away, and the remainder thoroughly mixed and placed in a perfectly clean dry bottle. A half-inch Morse twist-drill is the best for general use. In taking samples of pig-iron, the loose sand should be carefully removed from the outside of the pig and a piece of stout paper wrapped around it to prevent the sand and slag from the outside getting mixed with the clean drillings, which are received on a piece of glazed paper turned up at the edges. Drillings from pig-iron can be best mixed by rubbing them up in a small porcleain mortar. At blast-furnaces, to save the trouble of breaking pieces from the pigs, the arrangement shown in Fig. 3 is very convenient, as half a pig can be placed in the press. The framework is securely bolted to the table on which the press stands, and the pig is secured by means of the iron clamps. By removing the pieces of wood under the pig it is lowered so that two or three holes can be bored in different parts of the face of the pig to get an average. By taking one pig from the first bed, one from the last, and one from an intermediate bed, a good average of each cast may be obtained. When the ore varies, or when mixtures of different ores are used, these precautions are very necessary to get a sample that will really represent an average of the cast.

FIG. 3.

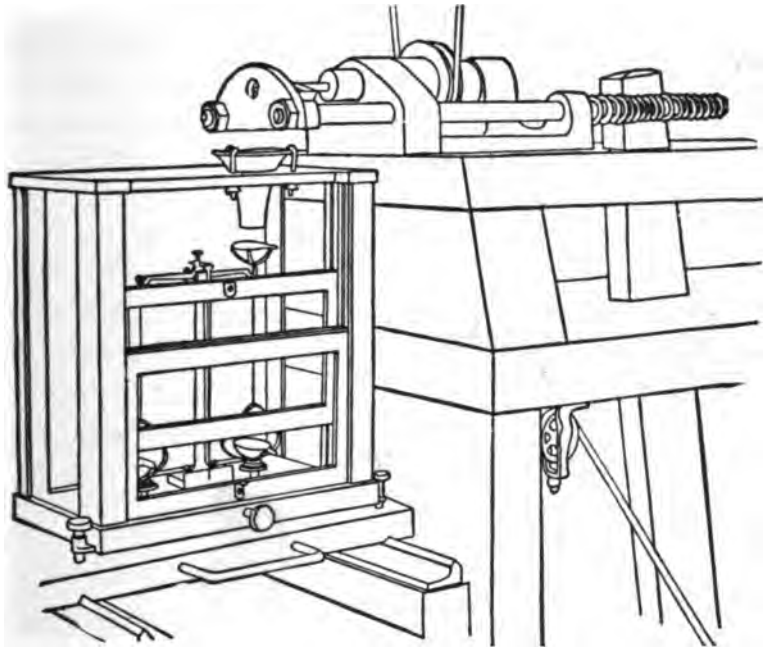


Drillings from large ingots must be taken by means of an ordinary brace.

Fig. 4 shows an apparatus for the drilling and weighing of samples of steel for colorimetric carbon or other rapid determinations, designed by Mr. Maunsel White, and in use at the laboratory of the Bethlehem Iron Company. The drill is mounted above the balance, the point of the drill directly overhanging the balance-pan. The piece to be drilled is placed

against the semicircular plate carried by the two rods that pass through the drill-frame; on the rear end of each rod is a coiled spring which supplies the pressure necessary for drilling. The rear ends of the rods are held together by a tie-piece, which is connected to a lever operated by the

FIG. 4.



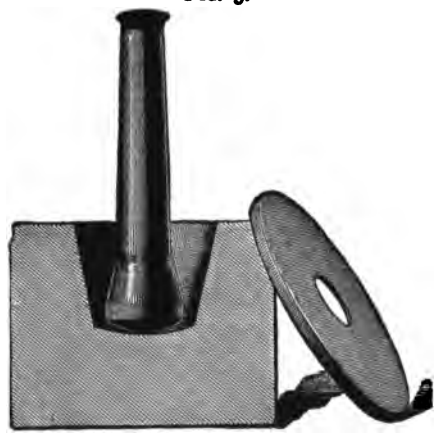
foot, so that the rods and plate can be forced forward for the reception of the piece to be drilled.

The balance is supplied with an overhead pan which receives the drillings guided to it through the funnel fixed in the top of the balance-case for this purpose. When the pan falls, showing that sufficient sample has been drilled, pressure is applied to the lever by the foot and the piece taken out. The balance-case rests upon an iron plate grooved on the bottom; these grooves engage with guides screwed to the table and permit the balance-case to be pulled forward, which facilitates the cleaning of the funnel from all clinging particles. This operation is done with a camel's-

hair brush or a feather. A magnet is run around in the lower pans to guard against the chance of falling particles interfering with the accuracy of the weights. The upper door of the balance-case is then lowered into the position shown in Fig. 4, which gives free access to the upper pan containing the sample. The sample is now accurately weighed, the pan lifted out, and the drillings transferred to the test tube.

The use of a ¼-inch twist-drill has been adopted and found to give good results. The pans and funnel are aluminum and the bearings agate; the beam is short, 5½ inches in length, in consequence of which the weighing is done rapidly.

FIG. 5.



In taking samples of spiegel or of white-iron, small clean pieces from a number of pigs should be taken and powdered in a hardened steel mortar. The mortar shown in the sketch (Fig. 5) is forged from high carbon steel, hardened, and the temper drawn from the outside. This makes the mortar both hard and tough. The sheet-iron cover prevents the pieces from flying. The face of the pestle is very hard, and the handle comparatively soft, so that it will not break when struck by the hammer.

In taking samples for analysis, when the method used requires the sample to be in a fine state of subdivision, the very fine part of the sample should never be separated from the coarser particles by a sieve or screen, but the sample should be mixed thoroughly, and a portion, fine and coarse together, taken and powdered, so that all may pass through the sieve.

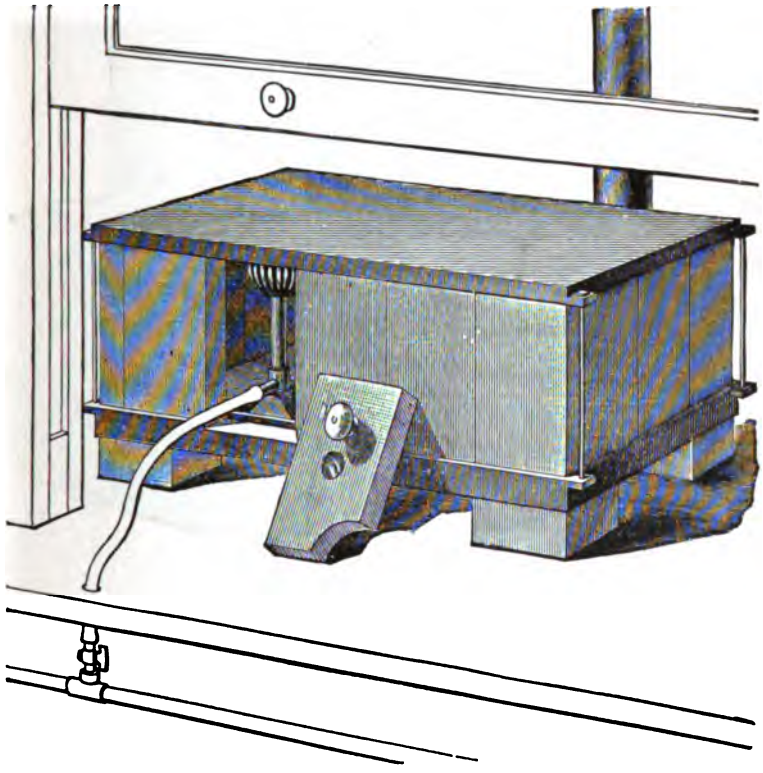
GENERAL LABORATORY APPARATUS

Hot Plate and Air-Bath

Fig. 6 shows a very convenient form of hot plate, and Fig. 7 an air-bath. This air-bath is made from an ordinary cast-iron sink, which is

supported on fire-bricks. The top is of asbestos board, with a piece of sheet-iron underneath to strengthen it. The holes are large enough to take the largest-sized beakers, while the smaller beakers are supported by asbestos rings. An ordinary gas-regulator or governor, which supplies the gas at a constant pressure, keeps the temperature sufficiently uniform.

FIG. 6.

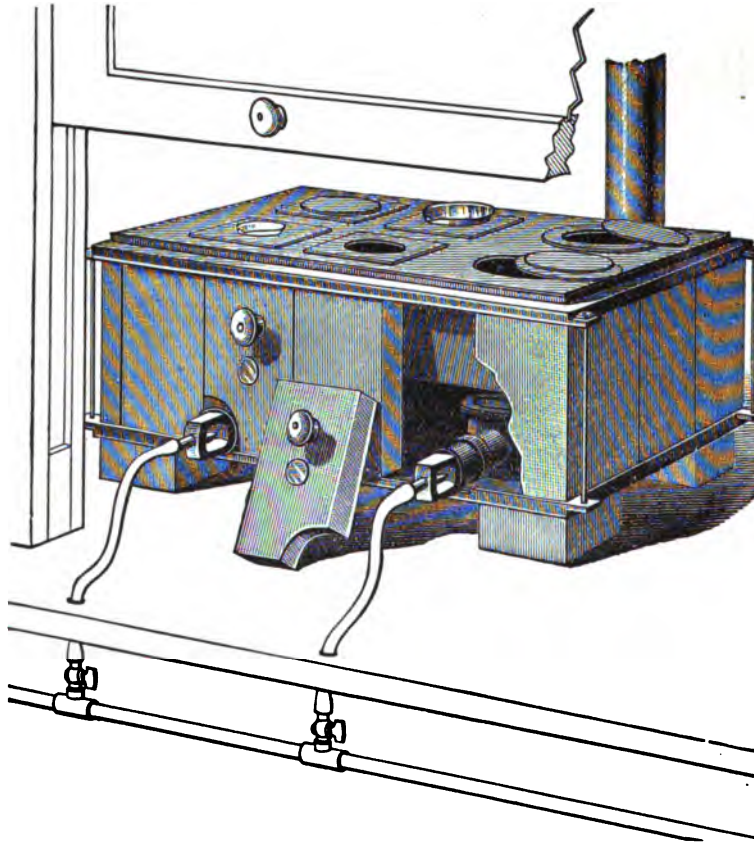


Evaporations may thus be effected with great saving of time and with little danger of loss by spirting. The products of combustion of the gas are carried off by a separate flue, and the sulphuric acid formed does not come in contact with the solutions in the baths.

The hot plate is generally used instead of a sand-bath, the surface of the iron being kept clean and free from rust by an occasional coat of stove-polish. Evaporations on the hot plate may be hastened by standing

the beaker containing the solution inside another beaker with the bottom cut off. Beakers may readily be cut in this way by starting a crack and leading it around with a red-hot iron or glass rod. For evaporating solutions in capsules or dishes a beaker cut off in this way and placed

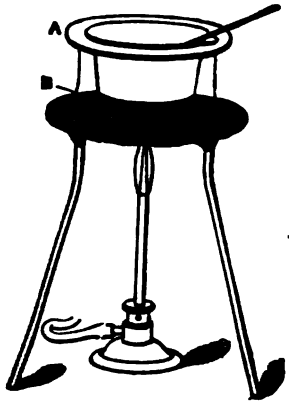
FIG. 7.



on a tripod covered with wire gauze, as shown in Fig. 8, may be used with great advantage. The capsule is supported on an asbestos ring, A, the bottom being about ½ inch (12 mm.) from the wire gauze. A piece of thin asbestos board, B, about ¾ inch (18 mm.) in diameter, rests on the gauze and covers the point of the flame of the Bunsen burner, and,

by throwing the heat more on the sides of the capsule, tends to prevent spirting when the solution in the capsule gets thick and pasty. A piece of heavy asbestos board of the proper width and length bent in a circle and wired may take the place of the broken beaker.

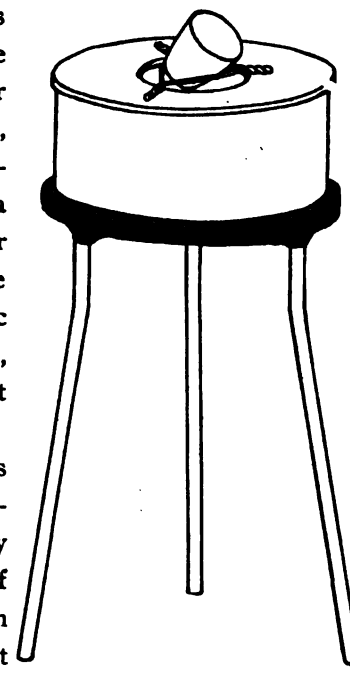
FIG. 8.



Apparatus for Hastening Evaporations

The little piece of apparatus shown in Fig. 10 was designed by Mr. J. E. Whitfield and is most useful in hastening evaporations. It consists of a platinum tube $^{3}/_{16}$ of an inch in diameter, coiled above the burner to present more heating surface, through which passes a blast of air. As the platinum tube and Bunsen burner are both supported on the arm of the stand, the level of the tube may be made to accommodate itself to a crucible on a stand, to a capsule on a tripod (Fig. 8), or to a beaker on the air-bath. In the treatment of the insoluble residues from ores by hydrofluoric and sulphuric acids it is quite invaluable, as it not only hastens the evaporation but prevents loss by spirting.

FIG. 9.



The blast of hot air breaks the bubbles on the surface of the liquid, and when properly directed it gives the liquid a rotary motion that tends to throw onto the sides of the crucible any particles of the liquid thrown up by the bubbles. The amount of heat that can be applied to a crucible under these circumstances, without causing loss, is really surprising. It is equally useful when evaporating solutions in beakers on the air-bath or hot-plate. In laboratories where a blast of air is always at command, the principle may be applied in many ways for hastening evaporations.

FIG. 10.

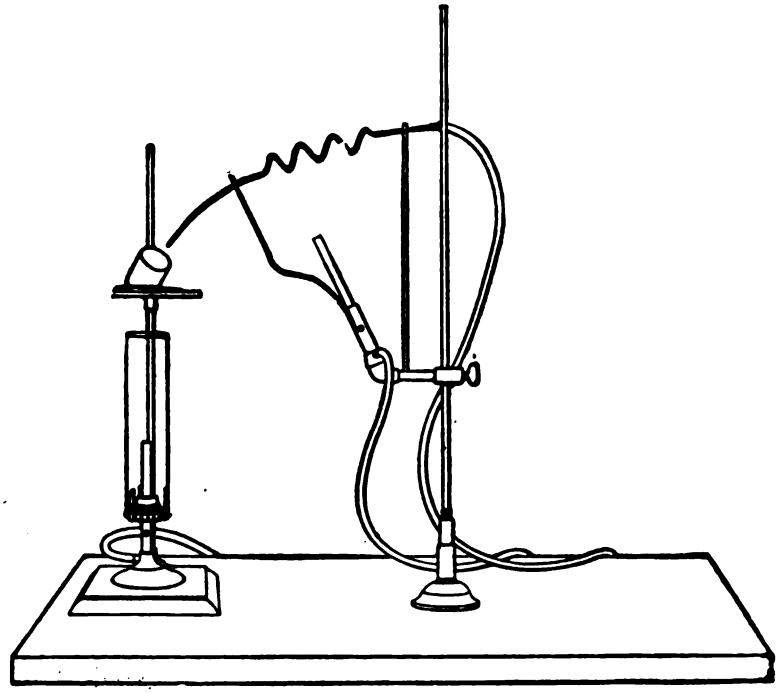


FIG. 11.

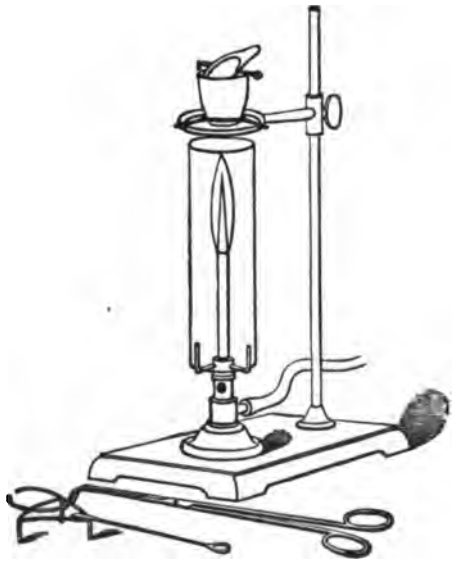


FIG. 12.

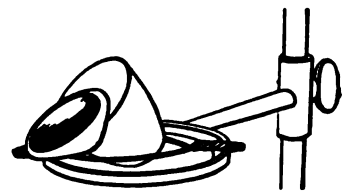
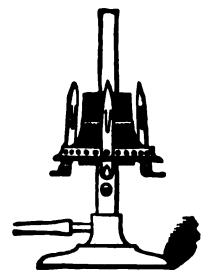


FIG. 13.



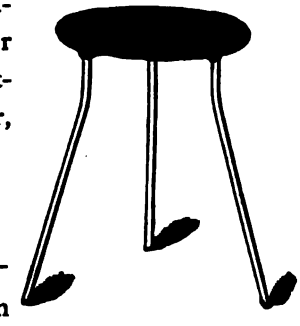
Even a cold blast of air from a drawn-out glass tube directed on the surface of a liquid hastens the evaporation very materially.

The arrangement shown in Fig. 9 is very useful for such work as volatilizing silica by hydrofluoric and sulphuric acids in the presence of large precipitates such as tungstic acid. The evaporation may be carried on rapidly with practically no danger of loss by spirting as the heat is well diffused.

Igniting Precipitates

For ignitions, a Bunsen burner with a ring to regulate the supply of air, provided with an ordinary glass chimney, as shown in Fig. 11, is most convenient. By shutting off the air entirely a very low heat may be obtained, which is not rendered variable by air-currents, and the heat of the full flame of the burner is increased by the greater draft caused by the chimney and the perfect steadiness of the flame. By using a small platinum rod or wire to support the cover of the crucible, as shown in Fig. 11, a gentle current is induced in the crucible, which, while it greatly facilitates burning off carbon, is not sufficiently strong to cause loss by carrying off even the lightest ash. The crucible may also be inclined on its side, as in Fig. 12, the heat in this case being applied near the top of the crucible. Fig. 13 shows an easy method of fitting a chimney to a Bunsen burner by means of a cork and an ordinary Argand chimney-holder. When a higher temperature than that obtainable by a Bunsen burner is required, a blast-lamp, worked by a foot-bellows, by a water-blast, or by a small blower, is used.

FIG. 14.



Tripods

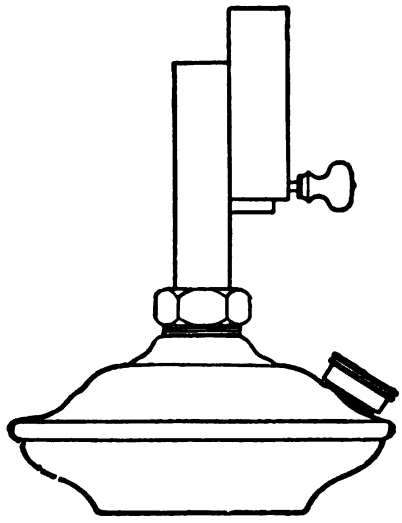
The most convenient arrangement for heating liquids in beakers, flasks, etc., is the iron tripod (Fig. 14). It consists of a cast-iron ring with three legs of heavy iron wire ¼ inch (6 mm.) in diameter. The ring is covered with brass wire gauze, 40 meshes to the inch, which can be replaced when it is burned out, but which lasts a long time. The vertical height of the tripod is about 7½ inches (191 mm.). A very convenient form of burner is

the Finkner ratchet-burner, as the flame can be raised or lowered by means of the ratchet on the burner, thus avoiding the necessity of reaching back over the table to the gas-cock. As the air and gas are both turned off at once, there is less danger of the flame blowing out when it is turned very low.

Gasoline and Alcohol Lamps

When illuminating gas is not obtainable for heating purposes, recourse must be had to gasoline or alcohol. If a gasoline gas machine is available it furnishes a fair substitute for ordinary illuminating gas, but special burners must be used. These will be found described in any dealer's catalogue. Sometimes, however, it is necessary to depend on gasoline alone as a source of heat, and in this event the best burner for general use is the Dangler lamp, which can be used for heating solutions and also for making ignitions and for fusions. This lamp is made on the principle of the plumber's torch or melting pot.

FIG. 15.



Alcohol is too expensive for general use for heating purposes, but for fusions for the determination of sulphur its use is advisable on account of the presence of sulphur compounds in gas. There are many patterns of alcohol lamps; among others, Barthel's lamp of the form shown in the cut (Fig. 15) may be mentioned.

Muffles

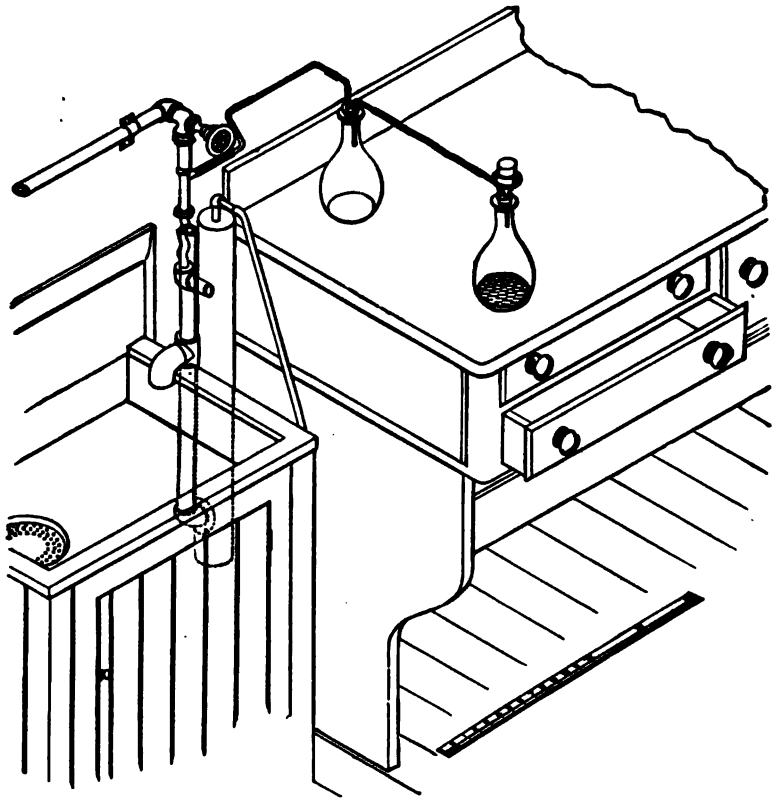
Some analysts prefer to make ignitions in a muffle, and where no gas is available it certainly offers many advantages.

Any good form of muffle furnace heated by gasoline, coke, or coal may be used for this purpose, but the muffle should not be less than 4 or 5 inches in height. The waste heat may be used for a hot plate or an air-bath.

Filter-Pumps

The use of filter-pumps for Bunsen's method of rapid filtration is now very general, and greatly facilitates many operations. The kind of pump is usually determined by the water-supply. With a good pressure of

FIG. 16.



water, the most convenient form of pump is the injector. Fig. 16 shows the Richards injector united with an air-cylinder, from which a current of air sufficient for an ordinary blast-lamp may be obtained. When the pump is used for filtering strong solutions of nitric acid a glass injector may be used, and the water allowed to flow at once into the sink or waste pipe. When the pressure of water is not great enough for an injector the Bunsen pump may be used, the vacuum obtained of course depending

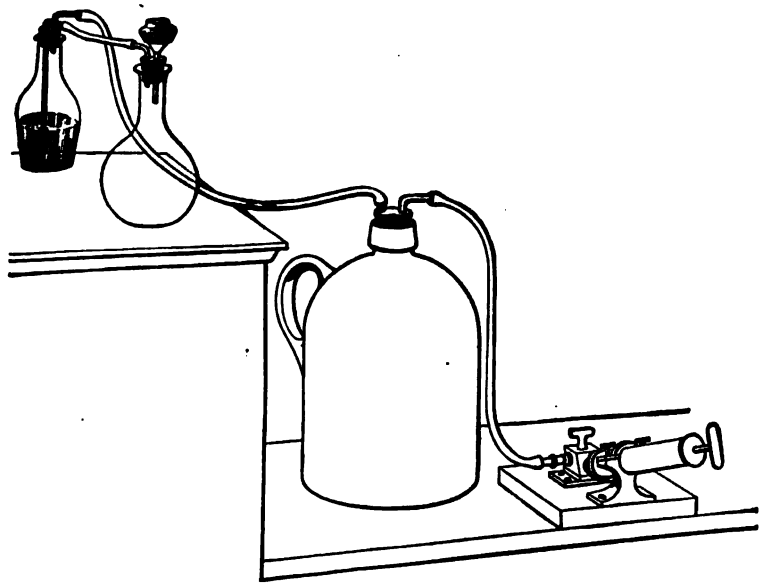
on the amount of fall. A tank with a ball-cock attachment makes this form of pump most convenient.

An ordinary air-pump may also be used for many purposes, but of course is unsuitable for filtering corrosive liquids, such as nitric acid, unless a wash-bottle containing a caustic alkali is interposed between the flask and the air-pump. The apparatus shown in Fig. 17 will give a very good idea of an arrangement which is very convenient when a water supply is not available. The jug, which may be of three or five gallons' capacity, serves as a reservoir. It connects directly with the air pump.

Bunsen's Method of Rapid Filtration

This method is too widely known to make a detailed description necessary, but some hints in regard to the details may be useful. In the

FIG. 17.



first place, it is very difficult to get good 60° funnels, so that the little perforated cones of platinum to support the point of the filter, which are sold by chemical dealers, rarely fit the funnel, and when they do not fit,

the filters are apt to tear. The small funnel of platinum foil, as recommended by Bunsen, can be made to fit the funnel better, but the edges sometimes cut the filter. A small funnel of parchment pricked full of pin-holes, and of the size and shape of the platinum-foil funnel, works very well. It is a mistake to use too great a pressure, especially at first, and the filter should be kept full. The filtering-flask should always be connected, not with the vacuum-pipe directly, but with another flask fitted with a little Bunsen valve, which allows the air to pass into the vacuum-pipe, but, in case of a sudden stoppage in the pump, prevents the back pressure from entering the filtering-flask and blowing out the contents of the funnel.

FIG. 18.

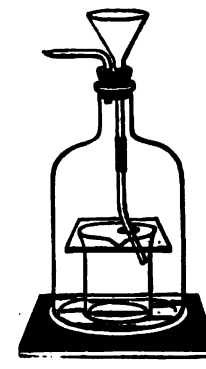


Fig. 18 shows an arrangement for filtering into a beaker instead of into a flask. It is necessary to have a glass cover over the beaker, as shown in the sketch, on account of the tendency the solution has to spatter, particles of the solution being carried out of the beaker in the current of air flowing into the vacuum-pipe.

Gooch's Method of Rapid Filtration

The pierced crucible and cone, with asbestos felt, devised by Gooch,* are almost indispensable to the iron analyst for the proper and rapid execution of many operations, as will be seen by the frequent references to them in the descriptions of the methods given farther on. Fig. 19 shows the crucible and cap, and Fig. 20 the cone. The asbestos, which should be of a soft, silky, flexible fibre, is scraped longitudinally (not cut) to a fine, soft down, purified by boiling in strong hydrochloric acid, and washed thoroughly on the cone. It may be dried and kept in a bottle. The perforated crucible is placed in one end of a piece of soft rubber tubing, the other end of which is stretched over the top of a funnel, as shown in Figs. 19 and 21. The neck of the funnel passes through the stopper of a vacuum-flask. To prepare the felt, pour a little of the prepared asbestos

*Proceedings Am. Acad. Arts and Sciences, 1878, p. 342 ; Chem. News, xxxvii, 181.

suspended in water into the crucible and attach the pump. The asbestos at once assumes the condition of a firm, compact layer, which is washed with ease under the pressure of the pump. After washing the felt, suck it dry on the pump, remove the crucible, detach any little pieces of fibre that may be on the outside of the bottom of the crucible, slip on the little cap, dry, ignite, and weigh. Remove the cap, place the crucible

FIG. 19. FIG. 20. FIG. 21.

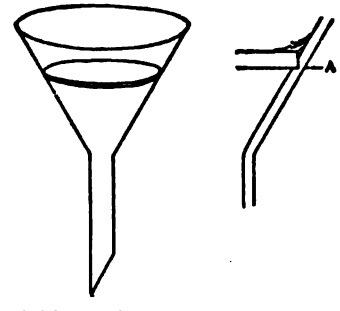
in the rubber holder, start the pump, and pour the liquid and precipitate to be filtered into the crucible, wash, dry, ignite, if required, cool, and weigh as before. The cone is fitted to a funnel by means of a rubber band stretched over the top of the funnel. The pressure of the pump pulls the cone down so that the overlapping part of the band forms a tight joint between the cone and the upper part of the funnel (Fig. 22). The felt is prepared in the same manner as in the crucible. Fill the cone with the asbestos suspended in water, start the pump, press down the cone into the funnel, and, if necessary, pour in more of the asbestos, letting it run all around from the upper edge of the cone so as to fill all the holes and make a firm, cohesive layer all over the inside of the perforated portion of the cone. Wash it well with water and suck it dry. It will then be ready for use. The cone is not intended for use when the precipitate is to be weighed, but, as it presents a very large filtering surface, it is most useful for such precipitates as manganese dioxide precipitated by Ford's method, etc. In this

FIG. 22.

case, when the precipitate has been washed and sucked dry, by removing the cone from the funnel and carefully separating the felt from the sides of the cone with a little piece of flattened platinum wire, it may be removed from the cone with the precipitate enclosed in it, and the whole mass transferred to a beaker or flask for re-solution. The cones may be of various sizes; for ordinary use, a cone 1¾ inches (45 mm.) in diameter is very convenient. They may also be used with a paper filter. In both the crucible and cones the holes should be very small, and drilled (not punched) as closely together as possible.

Perforated porcelain crucibles may now be obtained and are useful for many purposes such as the separation and weighing of ammonium phospho-molybdate precipitates. A porous alundum crucible is also in use and alundum plates of different degrees of porosity are very useful. These plates, which are circular and from 1 to 3 inches in diamater, should be carefully ground into a funnel (Fig. 23) so that they rest in the groove cut by the sharp edge of the plate. The space between the upper edge of the plate and the side of the funnel should be packed with asbestos. This is an excellent arrangement to use in filtering off the excess of sodium bismuthate in the determination of manganese by the bismuthate method, as the plate may be used a number of times without removing the excess of bismuthate.

FIG. 23.

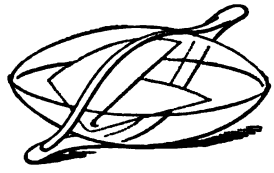


Counterpoised Filters

The Gooch crucible and felt are most useful for weighing precipitates which are to be dried and not ignited, as in the direct weighing of the phospho-molybdate of ammonium. When they are not available, however, recourse must be had to counterpoised filters. The best method for preparing and using them is as follows: Take two washed filters of the same size and about the same thickness, fold them as if about to fit them in funnels, and, by cutting from the upper edge of the heavier of the two with a pair of scissors, make them nearly balance. Place them between a pair of watch-glasses, as shown in Fig. 24, dry them at 100° C., and allow

them to cool is a desiccator. Place one in each pan of the balance, and, handling them with a pair of forceps, clip them until they balance exactly. Place each filter in a funnel, filter the precipitate on one of them, pass the *clear* filtrate (not the washings) through the other, and wash them both in the same manner. Remove them from the funnels, turning over the top edges of the filter containing the precipitate to prevent any of the latter from falling out, place them in a watch-glass, dry them at 100° C. (or at the required temperature, whatever it may be), cover them with the other watch-glass, cool in a desiccator, place them on opposite pans of the balance, and the weight added to the pan containing the empty filter, to make them balance, is the weight of the precipitate.

FIG. 24.



Filter Paper

All filter paper contains more or less inorganic matter, which remains, after burning the paper, as a white or brownish ash. The Swedish paper with the water-mark J. H. Munktell leaves the smallest amount of ash, and this ash contains from 35 to 65 per cent. silica, besides ferric oxide, alumina, lime, and magnesia in varying proportions.

Schleicher & Schull and Baker & Adamson prepare very pure filters by washing them with hydrochloric acid and hydrofluoric acid, and these should always be used for very accurate work. The commoner kinds of German paper contain much larger amounts of inorganic matter than the Swedish paper, which consists principally of calcium carbonate, but sometimes contains appreciable amounts of phosphates.

Washing-Bottles

Figs. 25*a*, 25*b*, 26, and 27 represent different forms of washing-bottles. Fig. 25*a* shows a bottle for use with ether or acids. The stopper is of glass. For ordinary use that represented in Fig. 25*b* is the best. The neck is wrapped with thin asbestos board, covered with a piece of wash-leather or chamois, which is sewed to keep it from slipping. This is very necessary when hot water is used. A piece of soft rubber tubing at A is more pleasant for the mouth than the glass, and after compressing the air in the

flask the tube can be grasped with the teeth, thus keeping up the stream of water for some time without effort. It also prevents the lips from being scalded when using very hot water. Fig. 26 shows a movable tip, which allows the stream of water to be directed by means of the finger. The form of flask shown in Fig. 26 is very convenient to use with ammonia-water, etc. The tube *a* is closed with the index finger, while the Bunsen valve *b* closing as soon as the air is compressed in the flask prevents the vapors from coming back into the mouth, and the stream of liquid is

FIG. 25*a*.

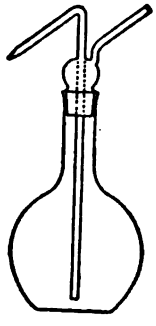


FIG. 25*b*.

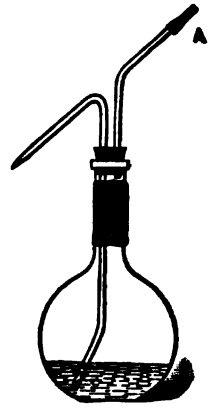


FIG. 26.

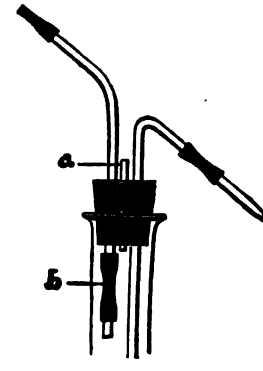


FIG. 27.

stopped instantly by removing the finger from *a*. Fig. 27 shows the Berzelius form, which is sometimes very useful. The air is compressed by blowing into the bottle through the jet, and by quickly inverting the bottle the stream of liquid is forced out until the equilibrium is restored. It requires a little practice to use this form of bottle easily, but when the art is once acquired it can be used with ammonia-water as well as pure water, and the facility with which it can be removed and pointed in any direction with the hand makes it most convenient for some purposes.

Removing Precipitates from Beakers

A feather trimmed in the way shown in Fig. 28 may be used to remove particles of adhering precipitates from beakers, evaporating-dishes, etc. A piece of soft rubber tubing on the end of a piece of glass rod or sealed glass tube is much more effective and convenient in most cases. It is

made by taking a short length of rubber tubing, placing a little pure caoutchouc dissolved in chloroform or naphtha in one end, squeezing the sides together between two pieces of board (Fig. 30), and allowing it to

FIG. 28.

FIG. 29.

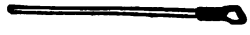
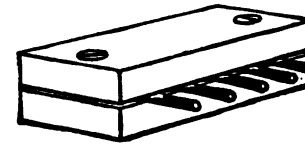


FIG. 30.

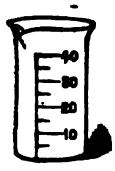


remain for at least twenty-four hours. It may then be trimmed down and placed on the end of a piece of glass rod or on the end of a piece of glass tubing having the ends fused together (Fig. 29). This little instrument has acquired the name of "policeman."

Measuring-Glasses

In adding reagents to a sample or to a solution, measured amounts should nearly always be used, and, as it is generally well under all circumstances to avoid adding them from the bottle direct, little beakers of the form shown in Fig. 31 are very useful. They can be graduated and marked by covering the side with a thin coating of paraffin, measuring in water from a burette, marking the levels and amounts in the paraffin with a sharp-pointed instrument, and etching them in the glass by filling the marks with hydrofluoric acid. After standing a few minutes the hydrofluoric acid may be washed off under the hydrant and the paraffin removed with hot water. As the amounts are intended to be only approximate, no great degree of care need be exercised in the graduation.

FIG. 31.



Caps for Reagent-Bottles

The stoppers and lips of reagent-bottles are very apt to become covered with ammonium chloride, dust, etc., when exposed in the laboratory, and especially such as are not in constant use,—volumetric solutions, stock-bottles, etc. It is well to keep them always covered with caps, which

may be bought from the dealers, or with cracked beakers, which answer the purpose nearly as well in most cases.

Rubber Stoppers

Rubber stoppers are now generally used instead of cork. Solid stoppers should always be purchased, and the holes cut with the ordinary cork-borers. This is readily done by moistening the cork-borer with water or alcohol. A little practice will enable any one to do this with great ease.

Desiccators

Crucibles should always be cooled in desiccators before weighing. The form shown in Fig. 32 is most convenient. The desiccator should contain fused calcium chloride. The crucible rests on a small triangle, which may be made of copper wire, each side being covered by winding a thin strip of platinum foil around it to prevent the crucible from coming in contact with the copper, which may become more or less corroded. Ni-chrome triangles may be used instead of platinum ones for ignitions and in desiccators.

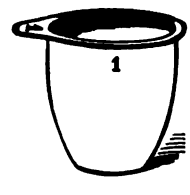
FIG. 32.

PLATINUM APPARATUS

Crucibles

The shape of the crucible is of considerable importance as regards its wearing properties. Fig. 33 shows the best form for general use. A crucible 1½ inches (38 mm.) high, $1\frac{5}{16}$ inches (33½ mm.) wide at the top, with a capacity of 20 c.c., and weighing with the lid about 25 grammes, is well adapted for weighing the usual precipitates found in the course of iron analysis. For fusions a much larger crucible is necessary: one $1\frac{13}{16}$ inches (46 mm.) high, $1\frac{13}{16}$ inches (46 mm.) wide on top, with a capacity of 55 c.c., and weighing about 60 grammes, will be found convenient and serviceable. Pure platinum is the best metal for crucibles. The iridium alloy, at one

FIG. 33.



time so popular, has not been found to wear well. It is stiffer than the pure metal, but much more liable to crack. The endurance of a crucible depends very much upon the treatment it receives. The salts of easily reduced metals fusing at a low temperature, such as lead, tin, bismuth, antimony, etc., should never be ignited in platinum; besides these, the phosphoric acid in some phosphates is occasionally partly reduced, rendering the platinum very brittle. A platinum crucible should never be bent out of shape when it can be avoided, and a wooden plug exactly the shape of the crucible (Fig. 34) is very useful to straighten it on when it has been bent. It should always be carefully cleaned before use: the precipitate last ignited should be dissolved in acid if possible, and the crucible washed out with water, dried, ignited, and cooled in a desiccator before weighing. A precipitate of ferric oxide will sometimes stain a crucible very badly; this stain may be removed by allowing the crucible to stand with cold hydrochloric acid for twelve hours. and then warming it for a short time. Stains that are not removed by hydrochloric acid may be removed by fusing potassium bisulphate in the crucible, or by fusing sodium carbonate in it, dissolving in water, and then treating the crucible with hydrochloric acid. Whenever a crucible begins to look dull and tarnished it should be cleaned inside and out with very fine sea-sand (not sharp sand) by moistening the finger, dipping it in the sand, and rubbing the crucible with it. This method of cleaning decreases the weight of the crucible very slightly, the sea-sand burnishing without cutting the crucible. It is very convenient to have each crucible and its cover marked with a number, as shown in Fig. 33.

FIG. 34.

Dishes

Fig. 35 shows a very convenient form of dish for the determination of silicon in pig-iron, silica in iron ores, etc. It is 3¼ inches (83 mm.) in diameter and 2¼ inches (57 mm.) high. Fig. 36 is for such work as precipitation of ferric oxide, etc. It is 5 inches (127 mm.) in diameter and $3\frac{5}{16}$ inches (84 mm.) high. The wire which is fused into the top of the dish

makes it much stiffer than it would otherwise be, and consequently it may be made lighter and cheaper than would be possible without the wire. The wire is hammered out and helps to form the lip. A platinum stirring-rod, formed from a piece of seamless tubing, rounded and fused together at the ends, is useful for many purposes. It may be from 5½ to 7 inches (140 to 179 mm.) long, ¼ inch (6 mm.) in diameter, weighing from 7.5 to 11 grammes.

FIG. 35.

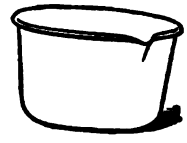
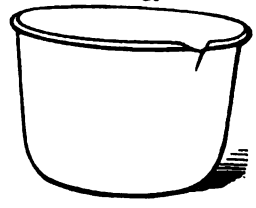


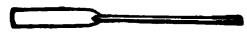
FIG. 36.



Spatula

Fig. 37 shows a very convenient and useful form of spatula. The blade, which is made of the platinum-iridium alloy, is fused into a tube of the same alloy which forms the handle. The weight of the spatula in the sketch is 14 grammes, length 6½ inches (165 mm.).

FIG. 37.



Triangles and Tripods

The triangles for supporting the crucibles during the ignition are shown in Figs. 11 and 12, as are also tripods for holding the lids, etc. These are made from wire about $\frac{1}{16}$ inch (1.6 mm.) diameter, the ends are fused, and the wire, where it is twisted, has the parts in contact fused together almost to the inside of the triangle, which makes it much stiffer. The triangles should be attached to the iron rings of the supports with a few turns of fine platinum wire. Ni-chrome triangles and tripods have largely replaced platinum.

Crucible-Tongs

Fig. 38 shows the best form of crucible-tongs. The part from *a* to *b* is of platinum, the straight part from *a* to *c* fitting over the end of the iron. The surfaces at *d* are in contact when the tongs are closed, and with this portion the lid can be handled, and the crucible is clasped by the curved ends, which hold it firmly without danger of bending the crucible. They

are especially useful in handling a crucible containing a liquid fusion. Another form, shown in Fig. 39, is generally of brass, the points and bend

FIG. 39.

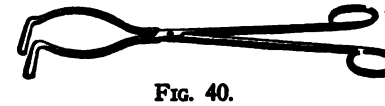


FIG. 38.

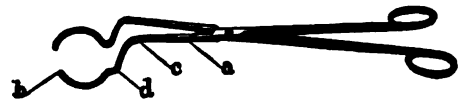
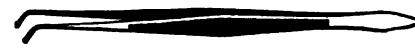
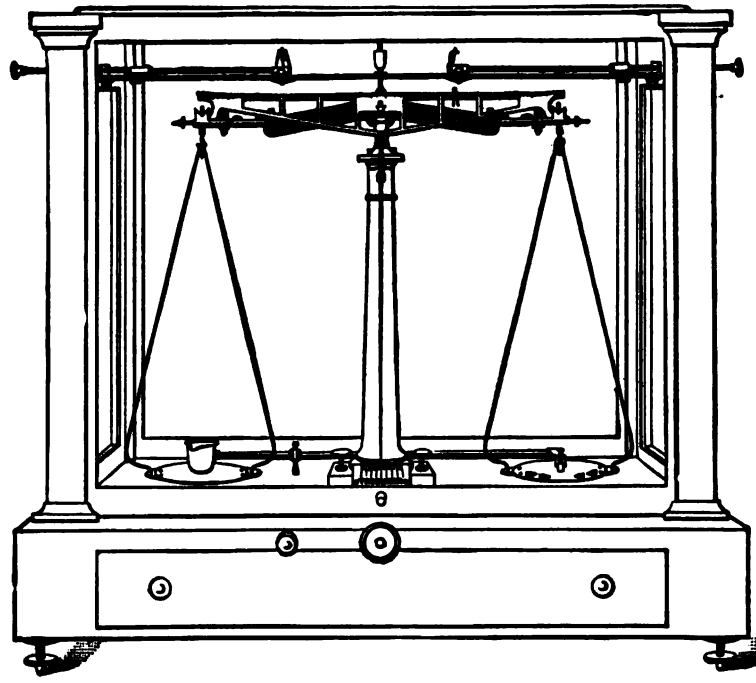


FIG. 40.



being lined with platinum. A small pair of forceps (Fig. 40) is useful for taking the crucible from the desiccator and placing it on the balance, the lid of the crucible being slipped a little to one side to allow one of the points of the forceps to go inside the crucible.

FIG. 41.



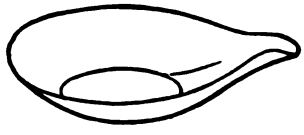
Balances

The balance is one of the most important things in the equipment of a laboratory, and a cheap balance is nearly always a very poor investment.

The quality of balances has improved greatly in the last few years, and it is now possible to get a most admirable instrument of this kind at a comparatively low price. Fig. 41 shows a balance which for sensitiveness and quickness is unsurpassed. It is made to carry up to 200 grammes in each pan. The beam is of aluminum, as are also the pans. The stirrups are of nickel, the knife-edges and bearings of agate, while the arrangement for carrying the riders (Fig. 42) is most ingenious and effective. It is of course very convenient to have one balance for weighing crucibles, etc., and another for weighing samples for analysis. The balance for the latter purpose may be much smaller than the balance for the former, and should be provided with a small aluminum pan with a spout (Fig. 43), to facilitate the transfer of samples to flasks, test-tubes, etc. The pan should have a counterpoise. A pair of small forceps, slightly magnetized, may be used to advantage in getting exact weights of steel drillings, and a camel's-hair brush is necessary to detach small particles of ore, etc., from the aluminum pan or balanced watch-glasses.

FIG. 42.

FIG. 43.



Factor Weights

The use of factor weights is in many cases extremely convenient, as it does away with all calculation, and is to that extent time-saving and valuable in avoiding one source of error. Thus, in determining carbon by combustion in steel, using 2.7273 grammes of the steel, 0.1 milligramme of carbonic acid is equal to 0.001 per cent. of carbon in the steel. For deter-

mining silicon in pig-iron the ¼ factor weight, or 1.1732 grammes, is very convenient. When the weight of silica is multiplied by 4, one milligramme is equal to 0.01 per cent. of silicon. Or, for rapid silicon determinations, the $\frac{1}{10}$ factor weight, 0.4693 gramme, is used.

REAGENTS

Distilled Water

Several forms of apparatus for distilling water may be obtained from dealers, so that no description is necessary in a work of this character. Distilled water being used in much larger amount than any other reagent, it should be carefully tested from time to time, and care should be taken to see that it is free from sulphates, chlorides, and anything else that may be carried over during the process of distillation. Long boiling of distilled water in wash-bottles is to be avoided, for no matter how resistant the glass may be, small amounts of silica will in time be dissolved by the water and carried down with such precipitate as ferric oxide, alumina, etc.

ACIDS AND HALOGENS

Hydrochloric Acid. HCl. Sp. gr. 1.2

Chemically pure hydrochloric acid is readily obtained. It should be free from chlorine, sulphuric and sulphurous acids, arsenic, and fixed salts. To test for sulphuric and sulphurous acids, evaporate 100 c.c. to dryness with a little pure potassium nitrate, redissolve in water with a few drops of hydrochloric acid, filter, if necessary, and add barium chloride. To test for arsenic, put into a clean dry test-tube a few centigrammes of pure stannous chloride, pour in carefully 6 or 8 c.c. hydrochloric acid, and gradually 2 or 3 c.c. pure sulphuric acid, shaking the test-tube gently. If the hydrochloric acid is free from arsenic the solution remains clear and colorless, but if arsenic is present the solution becomes yellowish, then

brownish, and finally metallic arsenic is deposited. The test-tube should be gently warmed if no reaction occurs at first. To test for chlorine, pour some of the acid into a solution of potassium iodide containing a little starch solution. A blue coloration indicates chlorine or ferric chloride. To test for metallic salts, neutralize about 100 c.c. of the acid with ammonia and add ammonium sulphide. To test for salts of the alkalies, evaporate about 100 c.c. of the acid to dryness, and test any residue which may remain.

Nitric Acid. HNO_3. Sp. gr. 1.41

Nitric acid should be free from nitrous acid, the presence of which may be known by the yellowish color it produces. It may be freed from this gas by passing a current of air through the acid until it becomes colorless. To test for hydrochloric acid or chlorine, dilute largely and add a solution of silver nitrate. To test for fixed salts, evaporate about 100 c.c. to dryness. The ordinary acid diluted with an equal volume of water gives the acid of 1.2 sp. gr. used to dissolve steel for the color carbon test. It should be carefully tested for chlorine and hydrochloric acid.

Sulphuric Acid. H_2SO_4. Sp. gr. 1.84

Sulphuric acid should be colorless. To test for oxides of nitrogen, Warington suggests placing about two pounds of the acid in a bottle, which it half fills, and shaking violently. The air washes the gases out of the acid, and the presence of the oxides of nitrogen may be detected by placing in the mouth of the bottle a piece of filter-paper saturated with potassium iodide and starch solution, which is colored blue when any of these oxides are present. To test for lead, supersaturate some of the acid with ammonia and add ammonium sulphide.

Hydrofluoric Acid. HFl

The use of ceresine bottles, suggested by Prof. Edward Hart, of Lafayette College, has made it quite possible to obtain pure hydrofluoric acid chemically pure and in any amount, so that it is no longer necessary to redistil the crude acid in the laboratory.

Acetic Acid. $H,C_2H_3O_2$ + Aq. Sp. gr. 1.04

Acetic acid of the strength given above is the best for use in iron analysis. It should give no residue on evaporation, and no precipitate upon neutralization with ammonia and the addition of ammonium sulphide. It should be free from phosphoric acid. To test it for phosphoric acid, evaporate 100 c.c. nearly to dryness, add a little magnesium mixture and a large excess of ammonia, cool in ice-water, and stir vigorously. When phosphoric acid is present, a precipitate of ammonium magnesium phosphate will be obtained.

Citric Acid. $H_3,C_6H_5O_7,H_2O$

Citric acid is easily obtained in a state of purity in the form of crystals having the above composition. It should be kept in the solid condition, and dissolved as needed. It is soluble in ¾ part of water at 15° C.

Tartaric Acid. $H_2,C_4H_4O_6$

Tartaric acid is also easily obtained sufficiently pure for use in iron analysis. The crystals should be dissolved only as needed. The only impurity is a small amount of lime. It is soluble in ½ part of water at 15° C.

Oxalic Acid. H_2,C_2O_4

Oxalic acid crystallizes from its aqueous solution as $H_2,C_2O_4,2H_2O$, soluble in 8.7 parts of water at 15° C. It loses its water of hydration very easily even at the ordinary temperature in dry air, and very quickly at 100° C.

Bromine. Br

Bromine is easily obtained in a condition sufficiently pure for use as a reagent. It is a dark brown, extremely corrosive liquid, of sp. gr. 2.97. It is soluble in about 30 parts of water at 15° C. It is best kept in a glass-stoppered bottle with a ground cap. As the aqueous solution is generally used, it is convenient to put only a small amount—say 20 or 30 c.c.—in the bottle, fill the bottle nearly full of cold distilled water,

shake it up well, and pour off the saturated solution as required. There usually remains in the bottom of the bottle a small amount of impurity, which is insoluble in water.

Iodine. I

Iodine is a metallic-looking crystalline solid, of sp. gr. 4.95. Resublimed iodine is not sufficiently pure for use, and must be redistilled with great care, unless it is used as iodine dissolved in iodide of iron, and filtered. To distil it, place about ½ kilo. in a large glass retort of about 2 litres' capacity connected with an adapter about 18 inches (456 mm.) long and 3 inches (75 mm.) in diameter at the largest part. The heat from a Bunsen burner turned quite low will cause the violet vapors of iodine to pass rapidly into the adapter, where they will condense without any means being taken to cool it. By gently warming the outside of the adapter after the distillation has been finished, the iodine may readily be detached in large masses and removed. It should be kept in a wide-mouth, glass-stoppered bottle.

Chlorine. Cl

Chlorine is a yellowish gas about two and one-half times heavier than air. It is sparingly soluble in water. When required it must be made. The details are given under "Determination of Silicon in Iron and Steel."

Sulphurous Acid. H_2SO_3

Sulphurous acid gas may now be obtained without difficulty in cylinders under pressure, and the aqueous solution or ammonium bisulphite easily made by passing the gas into water or diluted ammonia as required.

The gas, SO_2, has a specific gravity of 2.21 (air = 1). 1 c.c. of water at 15° C. dissolves 0.1353 gramme of SO_2.

Chromic Acid. CrO_3

Chromic anhydride as a red powder or in the form of scarlet crystals is easily obtained in a state of purity. It is deliquescent, and dissolves

in a small quantity of water, forming a dark brownish-colored liquid. It may be made by pouring 1 volume of a saturated solution of potassium bichromate into 1½ volumes of strong sulphuric acid, stirring constantly. The liquid on cooling deposits needles of chromic anhydride, which must be separated from the mother-liquid and purified by recrystallization.

GASES

Carbon Dioxide. Carbonic Acid Gas. CO_2

The best form of generator is shown in Fig. 44. It was first suggested by Casamajor.* It consists of a large tubulated bottle, the bottom of which is covered to the depth of about 1 inch (25 mm.) with buckshot, on top of which rest lumps of marble. Dilute hydrochloric acid (1 acid to 5 water) is admitted through the tube which enters at the tubulure at the bottom of the bottle, bending down so as to reach the bottom of the bottle. The wash-bottle A contains water. By blowing in the rubber tube attached to the acid-bottle the acid passes over into the tubulated bottle. When the stopcock K is closed, the pressure in the tubulated bottle forces the acid back into the acid-bottle. When the acid becomes exhausted and remains in the tubulated bottle, pour a little strong hydrochloric acid into the acid-bottle and blow it over into the tubulated bottle. The generated gas will force the liquid back into the acid-bottle, when it can be replaced by fresh acid. A slightly different form is shown in Fig. 47.

Hydrogen Sulphide Gas. H_2S

The same form of apparatus is used for generating hydrogen sulphide. Ferrous sulphide is substituted for marble, but hydrochloric acid is used instead of sulphuric acid, as is generally advised, for the ferrous sulphate formed crystallizes out and clogs the apparatus.

Hydrogen. H_2

The same form of apparatus as that used for carbonic acid and hydrogen sulphide can be used to advantage for generating hydrogen gas.

* American Chemist, vi. 209.

Pieces of zinc, which may be obtained by melting the zinc and pouring it in a sheet about ¼ inch (6 mm.) thick, so that it can easily be broken, are to be used, and not granulated zinc. Hydrochloric acid is better than sulphuric.

Oxygen Gas. O_2

Oxygen compressed in cylinders can be obtained from most dealers in chemicals, but it should always be carefully tested before being used for the determination of carbon in steel or iron, as the cylinders are sometimes filled with coal-gas, and a cylinder which has once held coal-gas is rarely free from hydrocarbons.

The gas may be made on a small scale in the laboratory by carefully mixing in a porcelain mortar 100 grammes potassium chlorate and 5 grammes powdered manganese dioxide, transferring to a retort, which the mixture should not more than half fill, and heating carefully over a Bunsen burner. The evolved gas may be collected in a gas-holder or in an india-rubber bag. The latter is not to be recommended for use for carbon determinations, as rubber is very liable to give off hydrocarbons.

ALKALIES AND ALKALINE SALTS

Ammonium Hydroxide. Ammonia. NH_4OH

The solution of ammonia gas (NH_3) commonly used is of sp. gr. 0.88, and contains about 30 to 35 per cent. of ammonia. It should be kept in glass-stoppered bottles and in a cool place, as the gas passes off very rapidly even at the ordinary temperature when open to the air. It should be colorless, leave no residue upon evaporation, be free from chlorides and sulphates, and give no precipitate with hydrogen sulphide.

Ammonium Bisulphite. NH_4HSO_3

Ammonium bisulphite is made by passing sulphurous acid gas into strong ammonia until the solution becomes yellowish in color and smells strongly of sulphurous acid. White crystals of the neutral sulphite $(NH_4)_2SO_3H_2O$, are first deposited; these are gradually dissolved by the

excess of sulphurous acid until the solution becomes quite clear, assuming a yellowish tint. By exposure to air ammonium bisulphite is gradually oxidized to sulphate. Old ammonium bisulphite always contains a small amount of hyposulphite, which occasions a precipitate of sulphur when deoxidizing solutions of ferric salts. It is not now difficult to purchase pure ammonium bisulphite, but sodium bisulphite is very apt to contain phosphoric acid. When made from strong ammonia-water, 18 c.c. of bisulphite will deoxidize a solution of 10 grammes of iron or steel.

Ammonium Sulphydrate. Ammonium Sulphide. $(NH_4)_2S$

Ammonium sulphide is made by saturating strong ammonia with hydrogen sulphide and adding an equal volume of ammonia. The reactions are

$$NH_4HO + H_2S = NH_4HS + H_2O \text{ and}$$
$$NH_4HS + NH_4HO = (NH_4)_2S + H_2O.$$

The solution becomes yellow by age or by exposure to the air.

Ammonium Chloride. NH_4Cl

Ammonium chloride is a white, crystalline, anhydrous salt, soluble in about its own weight of water at 100° C., and in 2.7 parts of water at 18° C. It volatilizes when heated without previous fusion. The salt is usually purified by sublimation. It generally contains a little iron, but is free from other impurities. To prepare ammonium chloride for use in J. Lawrence Smith's method for decomposition of silicates, dissolve it in boiling water and evaporate down on a water-bath or air-bath. When the salt begins to crystallize out, stir vigorously. The crystals formed will be very small. Drain off the liquid and dry. The salt can then readily be powdered.

Ammonium Nitrate. NH_4NO_3

Ammonium nitrate is a white, crystalline salt, soluble in one-half its weight of water at 18° C., and in much less at 100° C. When dissolved in water it produces great cold. By evaporation it loses ammonia and

becomes acid. When heated it fuses at 108° C., and is decomposed between 230° C. and 250° C. into water and nitrous oxide, $NH_4NO_3 = 2H_2O + N_2O$. It should leave no residue when volatilized.

Ammonium Fluoride. NH_4Fl

Ammonium fluoride may be made by saturating hydrofluoric acid by ammonia. The salt crystallizes when left to evaporate over quicklime. It is slightly deliquescent, and therefore difficult to keep, as the solution attacks glass.

Ammonium Acetate. $NH_4C_2H_3O_2$

Ammonium acetate is best made by slightly acidulating ammonia by acetic acid. One volume of strong ammonia-water requires about 2 volumes of acetic acid, 1.04 sp. gr., to neutralize it. It is best to make it as needed, as it decomposes when kept.

Ammonium Oxalate. $(NH_4)_2C_2O_4 + H_2O$

Ammonium oxalate is a white salt, crystallizing in long prisms united in tufts. It is soluble in 20 parts of water at 18° C.

Sodium Hydroxide. Caustic Soda. NaOH

Fused sodium hydroxide purified by alcohol is sufficiently pure for ordinary purposes. It forms white opaque masses, having a strong affinity for water. It dissolves in water with evolution of heat. Pure sodium hydroxide is prepared by allowing metallic sodium to decompose water in a platinum dish. It must be kept in a silver or platinum bottle, as the solution acts very rapidly on glass.

Sodium-Ammonium Phosphate. Microcosmic Salt. $NaNH_4HPO_4,4H_2O$

Sodium-ammonium phosphate (microcosmic salt) is a white, crystalline salt, soluble in 6 parts of cold and 1 part of hot water. It should not be kept in solution for any great length of time, as it attacks glass very readily. It loses its water of crystallization very easily, and when heated gives off its ammonia, leaving pure sodium metaphosphate, which in the

fused condition dissolves metallic oxides in many cases with the production of characteristic colors, which makes it a valuable reagent for blowpipe analysis. It is easily obtained in a state of purity.

Sodium Carbonate. Na_2CO_3

Sodium carbonate is never quite pure. It always contains small amounts of silica, alumina, lime, and magnesia, besides sulphuric acid. It may generally be obtained quite free from phosphoric acid. Every lot should be carefully examined for all the above impurities, and the amount per gramme noted, so that the proper subtraction may be made in each analysis. It is used in solution only for the neutralization of solutions, as in the determination of manganese by the acetate method, and, as the solution attacks glass very rapidly, it is best to dissolve the salt only as it is needed.

Sodium Bismuthate

Heat 20 parts of sodium hydroxide in a nickel or iron dish until all the water is expelled and the material is nearly red hot. Add in small quantities 10 parts of bismuth subnitrate previously heated until all the water and nearly all the nitric acid have been driven off.

To the fused mass add 3 parts of sodium peroxide and pour the brownish yellow fused material on an iron plate to cool. When cold, but before it begins to deliquesce, break it up and place it in a large jar of water to dissolve the excess of soda salts. Wash by decantation and finally on the pump in an alundum dish, or if this is not available, on a hard filter. Dry at a low heat and pass through a fine sieve.

Sodium Nitrate. $NaNO_3$

Sodium nitrate is used occasionally instead of potassium nitrate in making fusions of ores containing titanic acid. It may be prepared by acidulating a strong solution of sodium carbonate with nitric acid, heating until the water and excess of nitric acid are driven off, and powdering the dry salt.

Sodium Hyposulphite. Sodium Thiosulphate. $Na_2S_2O_3 + 5H_2O$

Sodium hyposulphite is very soluble in water, but decomposes even in tightly stoppered bottles, sodium sulphate being formed and sulphur precipitated. It should, therefore, be dissolved only as used.

Sodium Acetate. $NaC_2H_3O_2 + 3H_2O$

Crystallized sodium acetate dissolves in 3.9 parts of water at 6° C. It is rarely quite pure, containing, usually, calcium and iron salts, but it may be used after solution and filtration for partial analyses, as in the determination of manganese by the acetate method, etc. In complete analyses it is better to use ammonium acetate. When the use of sodium acetate is unavoidable, it can be made by dissolving C. P. sodium carbonate in acetic acid, boiling off the liberated carbonic acid, and adding acetic acid to slight acid reaction.

Potassium Hydroxide. Caustic Potash. KOH

Potassium hydroxide purified by solution in alcohol, filtration, and subsequent evaporation to dryness and fusion, is quite pure enough for all the ordinary purposes of iron analysis. An aqueous solution of 1.27 sp. gr. is used to absorb carbonic acid in the determination of carbon in iron and steel, in the determination of carbonic acid in ores, etc. 300 grammes of fused potassium hydroxide dissolved in 1 litre of water will give a solution of about this strength.

Potassium Nitrite. KNO_2

Potassium nitrite is used to separate nickel and cobalt. It is difficult to buy the pure salt, but it is easily made, as follows: Heat 1 part of potassium nitrate in an iron dish until it is just fused, then add, with constant stirring, 2 parts of metallic lead. Raise the heat slightly to complete the oxidation of the lead, and allow the mass to cool. Treat the mass with water, filter from the lead oxide, pass carbon dioxide through the solution to precipitate the greater part of the dissolved lead oxide, and filter. To the filtrate add a little ammonium sulphide to precipitate the last traces of lead, filter, evaporate to dryness, and fuse in a

platinum dish to decompose any hyposulphite that may have been formed, and preserve the fused salt for use. Potassium nitrite is deliquescent.

Potassium Nitrate. KNO_3

Potassium nitrate is a white, crystalline salt, anhydrous, and soluble in 7½ parts of water at 0° C., and in 0.4 part of water at 100° C. It melts below a red heat to a colorless liquid, and at a red heat gives off oxygen gas more or less contaminated by nitrogen, being converted into potassium nitrite and potassium oxide. The salt may be purchased in a sufficient state of purity for all purposes of iron analysis, but, as it may contain small amounts of sulphuric acid, the amount should always be determined and the proper allowance made when it is to be used for the estimation of sulphur in ores.

Potassium Sulphide. K_2S

Potassium sulphide is made by passing hydrogen sulphide into a solution of caustic potash and filtering from any precipitated alumina or ferrous sulphide. It is used instead of the corresponding ammonia-salt when the solution contains copper, as copper sulphide is slightly soluble in ammonium sulphide.

Potassium Bichromate. $K_2Cr_2O_7$

Potassium bichromate is an orange-colored, anhydrous, crystalline salt, soluble in 20 parts of water at 0° C., and in 1 part of water at 100° C. It melts below a red heat to a transparent red liquid, crumbling to powder upon cooling. Heated with strong sulphuric acid it gives off about one-sixth its weight of oxygen gas, the reaction being $K_2Cr_2O_7 + 4H_2SO_4 = Cr_2K_2(SO_4)_4 + 4H_2O + 3O$. It is readily obtained in a state of purity, but should always be fused to destroy any organic matter before being used to determine carbon in iron or in ores.

Potassium Chlorate. $KClO_3$

Potassium chlorate is a white, crystalline, anhydrous salt. It is soluble in about 30 parts of water at 0° C., and in about 2 parts at 100° C.

It is readily decomposed by heat, first into a mixture of potassium chloride and perchlorate, a portion of the oxygen being set free, and at a higher temperature the perchlorate is decomposed, the remaining oxygen is given off and potassium chloride alone remains. It is easily obtained in a sufficient state of purity for use in iron analysis. Heated with nitric acid it yields potassium nitrate and perchlorate, water, chlorine, and oxygen, thus:

$$8KClO_3 + 6HNO_3 = 6KNO_3 + 2KClO_4 + 6Cl + 13O + 3H_2O.$$

Heated with hydrochloric acid it gives potassium chloride, water, and a mixture of chlorine peroxide and chlorine, called *euchlorine*, thus:

$$4KClO_3 + 12HCl = 4KCl + 6H_2O + 3ClO_2 + 9Cl.$$

Potassium Bisulphate. $KHSO_4$

Potassium bisulphate is a white, crystalline salt, soluble in about one-half its weight of boiling water. A large amount of water decomposes it into potassium sulphate and free sulphuric acid; even in the presence of a large excess of sulphuric acid the neutral salt crystallizes out, leaving free sulphuric acid in the solution. Potassium bisulphate melts at 197° C.; at higher temperatures it gives off water, leaving the anhydrous salt, and at a red heat it gives off sulphuric acid, leaving the neutral sulphate. It is difficult to obtain it very pure, but it may be made as follows: Dissolve potassium bicarbonate in water, filter, and from a graduated vessel add sulphuric acid until, after boiling off the liberated carbonic acid, the solution is neutral, or but very faintly alkaline to test-paper. Filter, if necessary, and to the filtrate add as much sulphuric acid as was added in the first place to neutralize the bicarbonate. Boil the solution down, and finally fuse the mass in a platinum dish. Cool it, and when it is almost ready to solidify pour it into another dish. Break it up, and preserve it in glass-stoppered bottles.

Potassium Iodide. KI

Potassium iodide is a white, crystalline, anhydrous salt, very soluble in water, and in dissolving it causes a fall of temperature in the solution.

It is soluble in about 0.8 part of water at 0° C., and in 0.5 part of water at 100° C. It is soluble in 6 parts of alcohol at the ordinary temperature, and, when dissolved, if the addition of hydrochloric acid does not turn it brown, it is free from iodate. A solution of 1 part of potassium iodide in 2 parts of water will dissolve 2 parts of iodine, but upon dilution some of the iodine is precipitated.

Potassium Permanganate. $KMnO_4$ (or $K_2Mn_2O_8$)

Potassium permanganate is a dark purple-red, anhydrous salt, crystallizing in long needles. It is soluble in 16 parts of water at 15° C. It is easily obtained very pure, but the solution should always be filtered through ignited asbestos, as paper has a strong reducing action on it.

Potassium Ferrocyanide. $K_4Fe_2(CN)_6 + 3H_2O$

Potassium ferrocyanide is a yellow, crystalline salt, soluble in 4 parts of water at 0° C., and in 2 parts of water at 100° C. It is used as a reagent to show the presence of ferric salts, which produce a blue coloration, caused by the formation of ferric ferrocyanide (Prussian blue).

Potassium Ferricyanide. $K_3Fe_2(CN)_6$

Potassium ferricyanide is a blood-red, anhydrous, crystalline salt, soluble in about 3.1 parts of water at 0° C., and in 1.3 parts of water at 100° C. The dilute solution, like that of the ferrocyanide, is yellow in color. Ferrous salts added to the solution give a blue coloration, due to the formation of ferrous ferricyanide, while ferric salts produce no change of color. The ferricyanide should never be kept in solution.

SALTS OF ALKALINE EARTHS

Barium Carbonate. $BaCO_3$

Barium carbonate prepared by precipitation is a soft white powder. It is difficult to obtain in a state of purity, but it is easily prepared by adding a solution of ammonium carbonate to a clear boiling solution of

barium chloride, and washing the precipitated barium carbonate with hot water, first by decantation and afterwards on a filter. The ammonium carbonate should, of course, be free from sulphate. The thoroughly washed barium carbonate should be transferred to a bottle and shaken up with water, in which condition it is ready for use. Barium carbonate is very slightly soluble in water, requiring, according to the different authorities, from 4,000 to 25,000 parts of water to dissolve it. It is poisonous.

Barium Acetate. $Ba(C_2H_3O_2)_2$

Barium acetate may be prepared by dissolving pure barium carbonate in acetic acid. It crystallizes with 1 or 3 molecules of water, but dried at 0° C., or exposed to the air, it effloresces and yields the anhydrous salt as a white powder. It is very soluble in water, dissolving in about 2 parts of water at 0° C., and in about 1 part at 100° C. When heated it decomposes into acetone and barium carbonate, thus:

$$Ba(C_2H_3O_2)_2 = C_3H_6O + BaCO_3.$$

Barium Chloride. $BaCl_2,2H_2O$

Barium chloride is a white, crystalline salt, soluble in about 3 parts of water at 15° C., and in about 1½ parts at 100° C. Heated to 100° C. it loses its water of crystallization, yielding the anhydride as a white mass, which melts at a full red heat. Barium chloride is almost insoluble in strong hydrochloric acid. It is used almost exclusively for the determination of sulphuric acid, and may be kept in solution for this purpose. 100 grammes of the crystallized salt dissolved in 1 litre of water is a good proportion to use. Of this solution 10 c.c. will precipitate 1.16 grammes of barium sulphate, equal to 0.4 gramme sulphuric anhydride or 0.16 gramme sulphur.

Caustic Baryta. Barium Hydroxide. $BaH_2O_2,8H_2O$

Barium hydroxide is a white, crystalline salt, soluble in 20 parts of water at 15° C., and in 3 parts of water at 100° C. The anhydride may be prepared by heating barium nitrate to redness in a platinum crucible,

raising the heat gradually at first to avoid loss from frothing. It attacks platinum, however, at a high temperature. The solution has a strong affinity for carbonic acid, absorbing it readily from the air, the barium carbonate so formed causing a scum on the surface of the solution. The solution attacks glass very strongly.

Calcium Chloride. $CaCl_2$

Crystallized calcium chloride loses all its water of crystallization at 200° C., yielding the white porous anhydrous chloride, which is very deliquescent. The anhydrous salt fuses at a low red heat, but is partly changed to oxide. For this reason the fused salt should never be used for drying carbonic acid gas in the determination of this gas, as some of it is taken up by the calcium oxide. A solution of calcium chloride containing 59 parts of the anhydrous salt to 100 parts of water boils at 115° C., a saturated solution at 179.5° C.

Calcium Carbonate. $CaCO_3$

Pure calcium carbonate, for use in Prof. J. Lawrence Smith's method for the determination of alkalies in silicates, is prepared as follows: Dissolve marble or calcite, free from magnesia, in dilute hydrochloric acid, add an excess of powdered marble, heat the solution, and add some milk of lime to precipitate magnesia, calcium phosphate, etc. Filter, heat the solution almost to boiling, and precipitate by ammonium carbonate. The calcium carbonate formed is very dense powder, which settles readily and is easily washed. Wash thoroughly, dry, and preserve for use.

METALS AND METALLIC SALTS

Metallic Copper

Metallic copper absorbs chlorine gas at ordinary temperatures, and is used in iron analysis to absorb any chlorine that may be given off during the combustion of the carbonaceous matter liberated by the action of solvents on iron and steel. It is used in the form of drillings,

which should be taken with a perfectly dry drill, and which should be free from oil and grease. The drillings should be kept in a stoppered bottle, and may be used as long as they are perfectly bright and clean.

Cupric Sulphate. $CuSO_4,5H_2O$

Cupric sulphate is a blue, crystalline salt, soluble in 2.7 parts of water at 18° C., and in 0.55 part of water at 100° C. The aqueous solution of the neutral salt is strongly acid to litmus-paper. The crystals of cupric sulphate effloresce on the surface when exposed to the air; heated to 100° C. they lose 4 molecules of water, and when heated to 200° C. they lose the remaining molecule. The anhydrous salt is a white saline mass, which is decomposed at a bright red heat, giving off sulphurous acid and oxygen and leaving cupric oxide. The anhydrous salt has a strong affinity for water, and also for hydrochloric acid gas. A solution of cupric sulphate dissolves metallic iron, the copper being precipitated from the solution at the same time in a spongy mass.

Anhydrous Cupric Sulphate. $CuSO_4$

The property anhydrous cupric sulphate possesses of absorbing hydrochloric acid gas makes it useful in the determination of carbon by combustion, and it is best prepared for this purpose as follows: Heat crystals of cupric sulphate, about the size of a coffee bean, in a porcelain dish until the blue color of the crystals disappears and they become white. Transfer while still hot to a dry, glass-stoppered bottle.

Anhydrous Cuprous Chloride. CuCl

To prepare the granulated salt for use as an absorbent of hydrochloric cid and chlorine in carbon determinations, moisten the ordinary powdered salt of commerce in a porcelain dish and rub it up with a glass rod into little lumps about the size of a coffee bean. Heat it gradually until the water is expelled and the lumps, which will be dark brown in color, harden. Transfer to a glass-stoppered bottle.

Cupric Chloride. $CuCl_2 + Aq$

To prepare cupric chloride for use in dissolving iron or steel for the determination of carbon, grind up equal weights of cupric sulphate and common salt in a porcelain mortar, and pour over the mixture a small amount of water heated to from 50° to 60° C. The liquid becomes emerald-green in color, and deposits upon evaporation sodium sulphate. Decant from the deposited salt and evaporate again until the solution is reduced to a very small bulk. Cool, and decant from the remainder of the sodium sulphate and the excess of sodium chloride. By further evaporation and cooling the cupric chloride may be obtained in the form of green crystals. These crystals are deliquescent. The solution should be diluted and filtered through asbestos.

Ammonium-Copper Chloride. $2(NH_4Cl),CuCl_2,2H_2O$

Potassium-Copper Chloride. $2(KCl),CuCl_2,2H_2O$

Ammonium-copper chloride is a bluish-green crystalline salt, quite soluble in water.

Potassium-copper chloride is bluish-green likewise and more soluble than the ammonium salt. The recent experiments of the American members of the International Steel Standards Committee have shown that ammonium-copper chloride is nearly always impure, from the presence of hydrocarbons in the ammonium chloride, derived probably from the gas liquor from which ammonia salts are distilled. These hydrocarbons unite with the carbonaceous residue liberated from steel and iron in the process of determining carbon, and of course vitiate the results. Several recrystallizations free the salt to a certain extent from this impurity. The use of the potassium salt is not open to this objection.

To prepare these salts proceed as follows: Dissolve 107 parts of ammonium chloride or 149.1 parts of potassium chloride and 170.3 parts of crystallized cupric chloride ($CuCl_2,2H_2O$) in water and crystallize out the double salt. Dissolve about 300 grammes of the double salt in 1 litre of water, filter through ignited asbestos, and preserve for use in glass-stoppered bottles.

Cupric Oxide. CuO

Cupric oxide, both fine and coarse, for combustions is easily obtained. It may be prepared as follows: Dissolve metallic copper in nitric acid, evaporate to dryness in a porcelain dish, transfer it to a Hessian crucible, and heat it in a furnace until no more nitrous fumes are given off. Keep the crucible well covered to prevent any coal getting into it, and avoid raising the heat too high, or the mass will fuse. Stir it from time to time, and when finished the oxide on top will be in a fine powder, while that in the bottom of the crucible will have sintered. Rub it up in a mortar and pass through a fine metal sieve. Keep the two kinds, fine and coarse, in separate glass-stoppered bottles, carefully covered to protect them from dust.

Ferrous Sulphate. $FeSO_4,7H_2O$

Ferrous sulphate (green vitriol, or copperas) is a bluish-green crystalline salt, soluble in 1.64 parts of water at 10° C., and in 0.3 part at 100° C. It is insoluble in alcohol. The crystals lose 6 molecules of water when heated to 114° C., but retain the last molecule even at 280° C. Heated to a red heat the anhydrous sulphate is decomposed, giving off sulphurous acid and leaving a basic ferric sulphate, which at a higher temperature is entirely decomposed, leaving only ferric oxide. To prepare the crystals for use in volumetric analysis, add alcohol to the aqueous solution of the ferrous sulphate, when the salt is precipitated as a bluish-white powder. Filter, wash with alcohol, dry thoroughly, and preserve in glass-stoppered bottles. The salt prepared in this way remains unaltered for a long time.

Ferrous-Ammonium Sulphate. $FeSO_4(NH_4)_2SO_4,6H_2O$

Ferrous-ammonium sulphate is a light green crystalline salt, soluble in 2.8 parts of water at 16.5° C. It may be prepared as follows: Dissolve 276 grammes of crystallized ferrous sulphate in water, filter, and add to the filtrate a clear solution of ammonium sulphate ($(NH_4)_2SO_4$, Glauber's Sal Secretum), evaporate down, and allow the double salt to crystallize out.

Drain the crystals, wash slightly with cold water, and dry on blotting-paper. When perfectly dry, preserve in a glass-stoppered bottle. The crystals remain unaltered for a long time even in moist air. They contain exactly $^1/_7$ their weight of metallic iron.

Mercurous Nitrate. $HgNO_3,H_2O$

To prepare mercurous nitrate, treat 40 grammes of metallic mercury in a covered flask with 25 c.c. strong nitric acid and 75 c.c. water. Boil the solution until all fumes of nitrous acid have disappeared and a small amount of mercury remains undissolved. Should all the mercury dissolve, add a little more and boil as long as any action continues. Cool the solution, pour it with the excess of mercury into a glass-stoppered bottle and add 100 c.c. of water and 5 c.c. of strong nitric acid. Keep an excess of mercury in the bottle, and if any crystals of mercurous nitrate separate out, dissolve them in water containing 5 per cent. of nitric acid.

Mercuric Oxide. HgO

Mercuric oxide is a light orange-yellow substance when prepared by precipitation from a mercuric salt. To a dilute solution of mercuric chloride add a slight excess of caustic potash, allow the precipitate to settle, wash it thoroughly by decantation with hot water, and finally wash it into a glass-stoppered bottle. It is used shaken up with water.

Lead Chromate. $PbCrO_4$

Fused lead chromate is a dark brown mass showing a radiated structure, and when powdered it is dark yellow in color, very heavy, and slightly hygroscopic. It is easily obtained very pure, but may be made as follows: Dissolve lead acetate in water, add a little acetic acid, filter, and precipitate by a solution of potassium bichromate. Wash by decantation, and finally on linen, dry, and heat in a Hessian crucible until the mass is just fused. Pour on a polished iron slab, grind in a clean mortar, and preserve the powder in glass-stoppered bottles, covered to exclude dust. Lead chromate heated to a full red heat gives off oxygen and is reduced to a mixture of basic lead chromate and chromium oxide.

Lead Peroxide. PbO_2

Lead peroxide is rather difficult to obtain in a state of purity; it is liable to contain lead nitrate and manganese oxide. The latter element interferes materially with its use as a reagent in the determination of manganese by the color test. It should always be carefully examined by boiling with dilute nitric acid, and if it imparts any color to the solution, must be promptly rejected. It may readily be prepared by digesting red oxide of lead in dilute nitric acid, decanting off the lead nitrate, and washing the residue thoroughly with hot water. By this treatment the red oxide is decomposed into lead protoxide, which dissolves in the nitric acid, and lead peroxide, which remains insoluble. Lead peroxide is a heavy brown powder, which, when heated, gives off oxygen and is converted into red lead or lead protoxide.

Lead Oxide Dissolved in Caustic Potash

Pour a cold solution of lead nitrate into caustic potash, 1.27 sp. gr., stirring constantly to dissolve the lead oxide, which precipitates. Add the lead nitrate until a permanent precipitate is produced. Allow this to settle, and siphon the clear liquid into a glass-stoppered bottle. It is well to coat the stopper with a little paraffin, to prevent its sticking.

Platinic Chloride Solution.

Dissolve platinum-foil in hydrochloric acid, adding nitric acid from time to time, evaporate to dryness on the water-bath, redissolve in hydrochloric acid, and evaporate again to drive off the nitric acid. Redissolve in water with the addition of a few drops of hydrochloric acid, filter, and preserve in a bottle the stopper and neck of which are protected by a ground-glass cap to prevent access of ammonia to the solution.

Metallic Zinc

Melt zinc, which should be as free as possible from lead and iron, in a Hessian crucible, and pour it in a thin stream from a height of four or five feet into a bucket of cold water, giving the crucible a circular motion

to prevent the zinc from falling in exactly the same place all the time. Pour off the water, dry the granulated zinc, and preserve it in bottles for use.

Zinc Oxide in Water

Emmerton * suggests the following method of preparing this reagent. Dissolve ordinary zinc white in hydrochloric acid, add the zinc white until there is an excess which will not dissolve, then add a little bromine-water, heat the solution, filter, and precipitate the zinc oxide by ammonia, being careful to avoid an excess. Wash thoroughly by decantation, and then wash into a bottle. Shake the bottle well, to diffuse the oxide through the water, before using.

REAGENTS FOR DETERMINING PHOSPHORUS

Magnesia Mixture

Dissolve 110 grammes of crystallized magnesium chloride ($MgCl_2 + 6H_2O$) or 50 grammes of the anhydrous salt in water, and filter. Dissolve 28 grammes of ammonium chloride in water, add a little bromine-water and a slight excess of ammonia, and filter. Add this solution to the solution of magnesium chloride, add enough ammonia to make the solution smell decidedly of ammonia, dilute to about 2 litres, transfer to a bottle, shake vigorously from time to time, allow it to stand for several days, and filter into a small bottle as required for use. 10 c.c. of this solution will precipitate about 0.15 gramme phosphoric acid.

Molybdate Solution

Weigh 100 grammes of pure molybdic anhydride, mix it thoroughly in a beaker with 400 c.c. of cold distilled water and add 80 c.c. of strong ammonia (0.90 sp. gr.). When solution is complete, filter and pour the filtered solution slowly with constant stirring into a mixture of 400 c.c. of strong nitric acid (1.42 sp. gr.) and 600 c.c. of distilled water. Allow to settle for 24 hours and filter. A solution prepared in this way will keep for several months even in hot weather without any deposition of molybdic acid.

* Trans. Am. Inst. Min. Engineers, x. 201.

METHODS FOR THE ANALYSIS

OF

PIG-IRON, BAR-IRON, AND STEEL

DETERMINATION OF SULPHUR

By Evolution as Hydrogen Sulphide

KARSTEN was the first to suggest dissolving iron or steel in hydrochloric acid, or dilute sulphuric acid, and collecting the evolved hydrogen sulphide by absorbing it in a solution of a metallic salt. He recommended cupric chloride.

Absorption by Alkaline Solution of Lead Nitrate

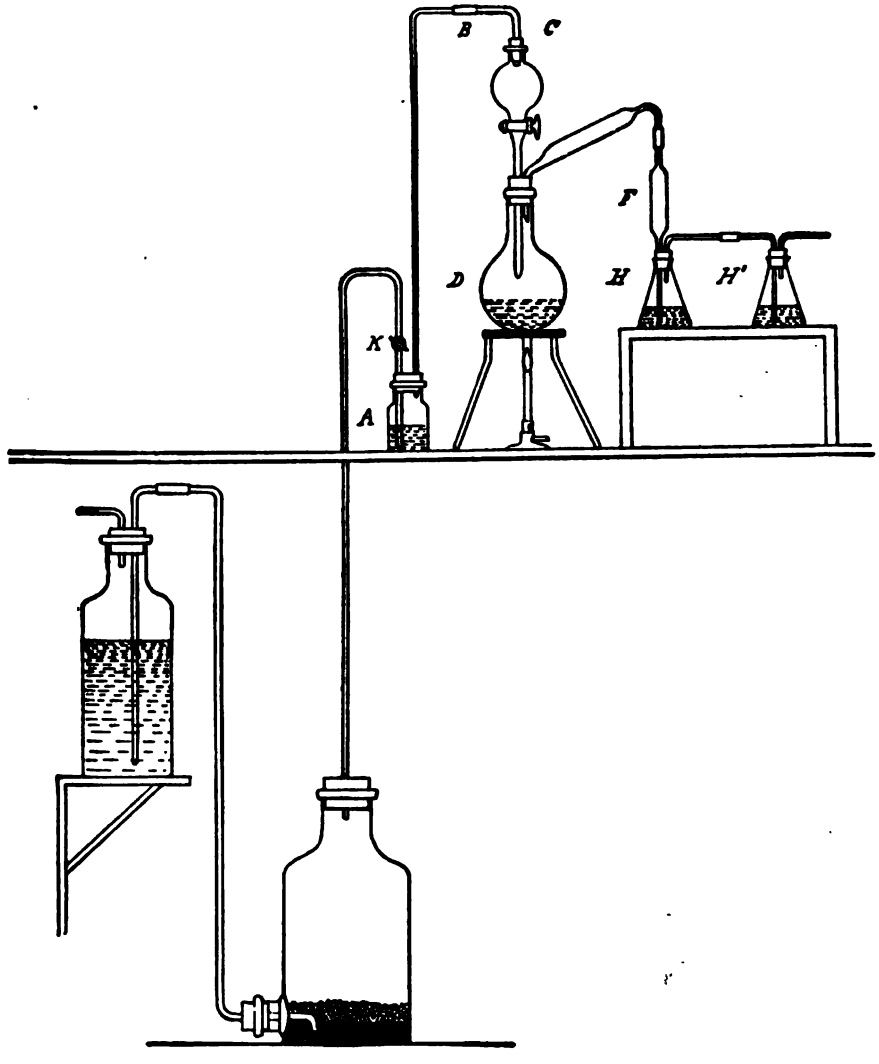
The apparatus, Fig. 44, shows the usual arrangement for carrying out the process, with the addition of the generating-bottles for supplying hydrogen gas. This is the apparatus described under the head of "Apparatus for Generating Carbonic Acid Gas," page 38. The wash-bottle A contains an alkaline solution of lead nitrate, and is connected with the funnel-tube by the rubber tube B, and a small piece of glass tubing, C, turned at a right angle with one end drawn down and covered with a short piece of rubber tubing. This fits in the neck of the bulb of the funnel-tube and makes a tight joint. The analytical process is conducted as follows:

Place 10 grammes * of borings or drillings, free from lumps, in the

* A 5-Factor weight (6.867 grammes) is a better amount to take, as, when the weight of barium sulphate found is multiplied by two, each milligramme is one-thousandth of a per cent. of sulphur.

previously dried flask D, and close it with the rubber stopper fitted with a funnel-tube and a delivery-tube. The outlet-tube from the flask D

Fig. 44.



connects with the tube F, reaching almost to the bottom of the Erlenmeyer flask H. Pour into each of the flasks H about 20 or 30 c.c. of

potassium hydrate solution of lead nitrate * and enough water to fill them two-thirds full. Connect the apparatus, and run a slow stream of hydrogen through until all the air is expelled, then close the glass stopcock of the funnel-tube, and shut off the supply of hydrogen by closing the small glass stopcock K. If the connections are all tight, the liquid will not recede in the tube F. When this is assured, disconnect the tube C, and fill the bulb—which should be of about 100 c.c. capacity—with a mixture of 50 c.c. of strong hydrochloric acid and 50 c.c. of water. Replace the tube C, turn on the hydrogen, and open the stopcock of the funnel-tube, so as to allow the acid to flow into the flask D. When the acid has all run into the flask, regulate the flow of the hydrogen so that the gas shall pass through the solutions in the flasks H, H′ as rapidly as possible, and heat the flask D. When the solution in the flask D has boiled for fifteen minutes, and all the metal has dissolved, remove the source of heat and continue the current of hydrogen for about ten minutes, regulating its flow by means of the stopcock K, to prevent any reflux of the liquid in H, which might be caused by the cooling of the flask D. Shut off the hydrogen, disconnect the apparatus, and wash the contents of the flask H into a 250 c.c. beaker. Unless a precipitate of lead sulphide appears in the second flask H′, it need not be emptied, but the same solution can be used over again for the next analysis. Collect the precipitate on a small filter, wash it once or twice with hot water, and, while still moist, throw the filter and precipitate back into the beaker, in which have been placed the instant before some powdered potassium chlorate and from 5 to 20 c.c. of strong hydrochloric acid, according to the amount of the precipitate of lead sulphide. Allow it to stand in a warm place until the fumes shall have partly passed off, then add about twice its volume of hot water, and filter into a 150 c.c. beaker. Wash with hot water, heat the filtrate to boiling, and add ammonia until the solution is slightly alkaline to litmus-paper. Acidulate with a few drops of hydrochloric acid, add from 5 to 10 c.c. of barium chloride

* See page 53.

solution,* boil 15 or 20 minutes, and stand aside for half an hour. Filter the precipitate of barium sulphate, preferably on a Gooch perforated crucible, wash with hot water, ignite, and weigh as barium sulphate, which contains 13.73 per cent. sulphur. It is always well to test the alkaline filtrate from the lead sulphide with a few drops of the lead solution, for it might happen that all the lead would be precipitated from the solution as sulphide, and an excess of hydrogen sulphide remain in the solution as potasium sulphide.

The entire operation described above can be performed in about two and a half hours.

Absorption by Ammoniacal Solution of Cadmium Sulphate

T. T. Morrell † passes the evolved gas into an ammoniacal solution of cadmium sulphate. Prepare a solution of cadmium sulphate of convenient strength, and add enough ammonia to redissolve the precipitate and give a clear solution. Place the solution in the bottles H, H′, and proceed as usual. Filter the precipitate of cadmium sulphide in a counterpoised filter, wash with water containing a little ammonia, dry at 100° C., and weigh as cadmium sulphide, which contains 22.19 per cent. of sulphur. Instead of cadmium sulphate, cadmium chloride seems to be now more generally in use.

Absorption by Ammoniacal Solution of Silver Nitrate

Berzelius proposed the use of a dilute solution of silver nitrate made alkaline by ammonia. The method of procedure is as follows. Dissolve 1 gramme of silver nitrate in a small quantity of water, and make it strongly alkaline with ammonia; pour about two-thirds of the solution into the first of the bottles H, and the remainder into the second, and fill up to the proper level with water. Proceed exactly as described above until the silver sulphide has been filtered off and washed. Dry this in precipitate carefully at a low temperature—say 100° C.—and brush it carefuly into a small, dry beaker, returning the filter to the funnel. Pour into the bottles H, should any of the sulphide remain adhering to the sides,

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* See page 47

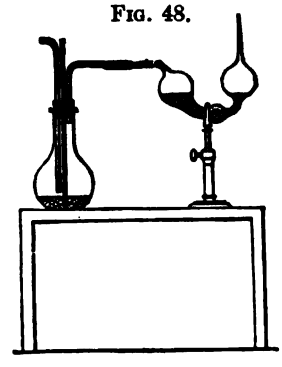
† Chem. News, xxviii, 229.

20 or 30 c.c. strong nitric acid, and when it is all dissolved, pour the acid in the filter, allowing it to run into the beaker containing the silver sulphide, and wash out the bottles with a little nitric acid, allowing this to run over the filter also. Digest the silver sulphide until it is all dissolved, then dilute with hot water, add an excess amount of hydrochloric acid, and filter off the silver chloride. Add a small amount of sodium carbonate and evaporate nearly dry, dilute, add a few drops of hydrochloric acid, filter if necessary, and precipitate as before by barium chloride. Even when the sample contains no sulphur a slight precipitate of silver carbide may be thrown down by the carburetted hydrogen evolved from the iron or steel by the action of the acid.

Absorption and Oxidation by Bromine and Hydrochloric Acid

Fresenius * suggested passing the evolved gases through a solution of bromine in hydrochloric acid, which has the advantage of oxidizing the hydrogen sulphide at once, but the disadvantage of filling the room with bromine-fumes unless the apparatus is placed under a hood with a good draft. It is necessary when using this method to avoid bringing the bromine-fumes in contact with rubber stoppers. Instead of the bottles H, attach to the exit-tube a bulb-tube of the shape shown in Fig. 45, containing from 3 to 5 c.c. of bromine and enough hydrochloric acid to fill the bulb-tube to the marks shown in the cut. When the operation is finished, wash the contents of the blub-tube out into a beaker, heat until the bromine is all driven off, neutralize by ammonia, and precipitate the sulphuric acid exactly as described on page 57. Instead of neutralizing by ammonia, the hydrochloric acid solution may be evaporated down nearly to dryness after adding a little sodium carbonate or the solution of barium chloride; but repeated experiments have shown that barium sulphate is practically insoluble in

FIG. 48.



* Fresenius, Zeitschrift, xiii. 37.

ammonium chloride, so that the plan of neutralizing by ammonia, being the shorter and less troublesome, is to be preferred.

Absorption and Oxidation by Potassium Permanganate

Drown * suggested the use of potassium permanganate solution as an absorbent and oxidizer, the process being carried on as follows: Make a solution of potassium permanganate, 5 grammes to the litre of water, and fill the bottles H to the proper height with this liquid, using three bottles, however, instead of two, and proceed with the operation as before described, being careful to avoid a rapid evolution of the gas. Wash the contents of the bottles H into a clean beaker, dissolve any manganese oxide that may adhere to the sides of the bottles in hydrochloric acid, add this to the solution in the beaker, and then add enough hydrochloric acid to entirely decompose the permanganate. Boil until the solution is colorless, filter if necessary, and precipitate by barium chloride. Allow it to stand overnight, filter, wash, ignite, and weigh the barium sulphate.

Absorption and Oxidation by Hydrogen Peroxide

Craig † suggested the use of ammoniacal solution of hydrogen peroxide in the absorbing-bottles. Attach to the exit-tube of the flask D (Fig. 44) a nitrogen-bulb of the usual form (Fig. 45), in which have been placed 4 c.c. of hydrogen peroxide and 16 c.c. of ammonia, and proceed as before directed. When the operation is finished, wash the contents of the nitrogen-bulb into a small beaker, acidulate slightly with hydrochloric acid, boil, add barium chloride, and determine the amount of barium sulphate as usual. As hydrogen peroxide always contains sulphuric acid, the amount must be carefully determined in each fresh lot of the hydrogen peroxide, and the proper correction made for the volume used.

By Oxidation and Solution

Most chemists still prefer for accurate work under all conditions the method of oxidizing and dissolving the metal and precipitating the sulphuric acid in the solution by barium chloride. The details are as

* Journal Inst. Min. Engineers, ii. 224. † Chem. News, xlvi. 199.

follows: Treat 5 grammes of drillings in a 600 c.c. beaker, covered by a watch-glass, with 40 c.c. of strong nitric acid. This requires care, for drillings of bar-iron and low steel are often acted on so violently, even by strong nitric acid, as to cause the solution to boil over. In this case it is best to place the beaker in a dish containing a little cold water and to add the acid gradually. When all the acid has been added and the action has ceased, some small particles generally remain undissolved, and their solution is effected by heating the beaker on the plate and finally by adding a few drops of hydrochloric acid. With pig-iron and steel there is usually no action in the cold, and in this case heat the beaker carefully until the action begins, then stand the beaker in a cooler place, and if the action becomes very violent, stand the beaker in cold water until it moderates. Very high carbon steels dissolve with great difficulty even in boiling acid; but the solution may be hastened by adding a few drops of hydrochloric acid from time to time. When solution is complete and only particles of graphite and silica remain undissolved, which is shown by the residue being entirely flotant, remove the cover, add a little sodium carbonate, and evaporate the solution to dryness in the air-bath. The addition of the sodium carbonate is to prevent any possible loss of sulphuric acid, which might otherwise occur by the decomposition of the ferric sulphate at a high temperature. Remove the beaker from the air-bath, and when cold add 30 c.c. hydrochloric acid, and heat until the ferric oxide is dissolved, evaporate again to dryness to render the silica insoluble, redissolve in hydrochloric acid, filter, wash and evaporate the filtrate until the ferric chloride begins to separate out, add 4 c.c. hydrochloric acid and a little water and dilute to 200 c.c. with hot water. Heat to boiling, add 10 c.c. saturated solution of barium chloride, and allow it to stand in the cold overnight. Filter, wash with a little very dilute hydrochloric acid, and finally with cold water; dry, ignite, and weigh as barium sulphate. If this ignited precipitate is reddish in color, it shows that ferric oxide has been precipitated with the barium sulphate. In this case fuse wth sodium carbonate, dissolve in water, filter, acidulate the filtrate, and precipitate as before. Or, filter the aqueous solution of the fusion, dissolve in hydrochloric acid, precipitate by ammonia, weigh the ferric oxide, and subtract from the weight of barium sulphate.

Bamber's Method (for Pig-Iron)

The investigations of Phillips * and Matthewman † have shown conclusively that in many pig-irons the evolution method fails to give the full sulphur contents. This seems to be due to the formation of organic sulphides, probably of the mercaptan series, and not to the presence of copper or arsenic, as has been supposed. As those compounds are quite volatile and very difficult to oxidize, some portions seem to pass through the absorbing solutions, while under certain circumstances other portions remain in the evolution flask with great persistency and are expelled only after long boiling. These difficulties are overcome by Bamber's method.

Dissolve 5 grammes or a 5-factor weight (6.866 grammes) in strong nitric acid, add 10 grammes of sodium carbonate, wash into a platinum or porcelain dish, evaporate to dryness and ignite over an alcohol flame. Treat with water with the addition of a little sodium carbonate. Acidulate with hydrochloric acid, evaporate to dryness, redissolve in water with a few drops of hydrochloric acid, and precipitate boiling with barium chloride.

Notes and Precautions

There are several precautions to be observed in using the oxidation method.

1. The sample should be dissolved in strong nitric acid, as, when dilute nitric acid, or even aqua regia, is used, some sulphur seems to escape oxidation.

2. The amount of acid in the solution from which the barium sulphate is precipitated must be most carefully regulated, as well as the absolute volume of the solution.

3. The reagents used must be examined for sulphuric acid. This is best done as follows: Measure into a beaker the total amount of acid, both nitric and hydrochloric, used in the determination, add a little sodium carbonate and evaporate to dryness. Redissolve in 15 c.c. of water and 5 or 10 drops of hydrochloric acid, filter, heat to boiling, add 10 c.c. of barium chloride, boil 10 or 15 minutes, allow to settle, filter, wash, ignite,

* Journal American Chem. Society, xvii. 891.

† Journal West of Scotland Iron and Steel Institute, iii. 27.

and weigh as barium sulphate. The amount found is to be subtracted from the total weight of barium sulphate found in the sample.

4. Many pig-irons contain appreciable amounts of titanium which separates out in the final evaporation. When this occurs the best method is to redissolve this precipitate by heating with strong hydrochloric acid, dilute with cold water to about 200 c.c., neutralize with dilute ammonia until the solution begins to darken and the ferric hydrate dissolves with difficulty, heat to boiling and precipitate with barium chloride.

5. When evaporating to dryness the temperature should not greatly exceed 100° C. and the heating should not be long continued, as even when sodium carbonate is added to the solution prolonged baking will undoubtedly cause loss of sulphuric acid.

6. Occasionally a pig-iron is met with that holds sulphur in the residue from the solution in nitric acid and evaporation with hydrochloric acid. To determine the sulphur in this insoluble residue after filtering and washing it, dry it carefully, transfer it from the filter to a platinum crucible, mix it with 5 grammes of potassium nitrate and 10 grammes of sodium carbonate and fuse it at a low temperature. Dissolve in water, filter, wash with hot water, acidulate the filtrate with hydrochloric acid and evaporate to dryness. Dissolve in water with a little hydrochloric acid, filter and precipitate the sulphuric acid with barium chloride. Filter, ignite and weigh. Add the sulphur obtained to the sulphur from the main filtrate.

Or instead of drying the insoluble matter, sprinkle the filter and precipitate with 5 grammes of potassium nitrate, place it in a crucible and heat until the paper is charred. Then add ten grammes sodium carbonate, fuse and proceed as before.

RAPID METHOD

Volumetric Determination by Iodine

This method, suggested by Elliott,* involves the evolution of the sulphur as hydrogen sulphide, its absorption in a solution of sodium

* Chem. News, xxiii. 61.

hydroxide, and titration by iodine in potassium iodide. It requires a standard solution of iodine, a standard solution of sodum thiosulphate, a starch solution, and a standard solution of potassium bichromate.

Iodine Solution

Dissolve 6.5 grammes pure iodine in water with 9 grammes potassium iodide, and dilute to 1 litre.

Sodium Thiosulphate Solution

Dissolve 25 grammes sodium thiosulphate in water, and dilute to 1 litre.

Starch Solution

Place in a porcelain or Wedgewood mortar 1 gramme of pure wheat starch, and rub it to a thin cream with water. Pour it into 150 c.c. boiling water, allow it to stand until cold, and decant the clear solution. The addition of 10 or 15 c.c. glycerine makes the solution keep better. It is better, however, to make a fresh starch solution every few days.

Dr. Waller recommends Müller's suggestion of grinding the starch with a strong solution of potassium or sodium hydroxide and dissolving in hot water for use. It keeps indefinitely.

Potassium Bichromate Solution

Dissolve 5 grammes pure potassium bichromate in water, and dilute to 1 litre.

All these solutions should be placed in glass-stoppered bottles and kept in a dark place.

Standardizing the Solutions

Standardize the bichromate solution as directed in the "Analysis of Iron Ores." When potassium bichromate is added to potassium iodide in presence of free hydrochloric acid, iodine is liberated, in accordance with the formula $K_2Cr_2O_7 + 6KI + 14HCl = 8KCl + Cr_2Cl_6 + 7H_2O +$ 61, or 1 equivalent of potassium bichromate $= 294.5$ liberates 6 equivalents of iodine $= 761.8$. Therefore, by adding to a solution of potassium

iodide in the presence of hydrochloric acid a known amount of bichromate, we can calculate the absolute amount of iodine liberated, and by titrating this solution by the thiosulphate solution we can accurately standardize the latter. The reaction which takes place when a solution of sodium thiosulphate is acted on by iodine is $2Na_2S_2O_3 + 2I = 2NaI + Na_2S_4O_6$, or 2 equivalents of thiosulphate unite with 2 equivalents of iodine to form sodium iodide and sodium tetrathionate. By adding a few drops of starch solution to a solution containing iodine, blue iodide of starch is formed, and colors the solution as long as it contains free iodine. When enough thiosulphate is added to a solution of this kind to combine exactly with the iodine, the blue color disappears. Conversely, upon adding a solution of iodine to a solution containing sodium thiosulphate and a little starch, the sensitive blue color of the iodide of starch will disappear as fast as formed until all the thiosulphate has been changed to tetrathionate, and then the first drop of iodine in excess will change the solution to a permanent blue. The same thing holds true as regards a solution containing free hydrogen sulphide, the reaction being $H_2S + 2I = 2HI + S$. Proceed therefore as follows: Dissolve about 1 gramme of pure potassium iodide in 300 c.c. water, add 5 c.c. hydrochloric acid, and then 25 c.c. of the bichromate solution, which will liberate a known amount of iodine. Drop in now the thiosulphate solution from a burette until the iodine nearly disappears, add a few drops of starch solution, and continue the thiosulphate until the blue color fades out entirely. The amount of iodine being known, the value of the thiosulphate solution is calculated from the reading of the burette. Now allow to flow into a beaker from a carefully graduated pipette 25 c.c. of the thiosulphate solution, dilute to 300 c.c., add a few drops of the starch solution, and drop, from a burette, standard iodine solution until the blue color is permanent. The value of the thiosulphate solution being known, that of the iodine solution is readily calculated. An example will illustrate this: Suppose we find by titration that 1 c.c. of our bichromate solution is equal to .00566 gramme metallic iron; then, as the reaction is $6FeCl_2 + K_2Cr_2O_7 + 14HCl = 3Fe_2Cl_6 + 2KCl + Cr_2Cl_6 + 7H_2O$, 1 equivalent of potassium bichromate = 294.5 is equal to 6 equivalents of iron = 335.4. Hence

335.4 : 294.5 = .0056 : .004969, or 1 c.c. of the bichromate solution contains .004969 gramme potassium bichromate, and consequently 25 c.c. contain .124225 gramme potassium bichromate. Then, as we saw by the formula that 294.5 parts bichromate liberate 761.8 parts iodine, we have 294.5 : 761.8 = .124225 : .32134, or 25 c.c. of the bichromate solution liberate .32134 gramme iodine. We now find that it requires 25.3 c.c. of the thiosulphate solution to decolorize the solution made by adding 25 c.c. bichromate solution to the potassium iodide; consequently each c.c. of the thiosulphate contains enough sodium thiosulphate to react with .0127 gramme iodine. We now measure out 10 c.c. of the thiosulphate solution, dilute it to 300 c.c., add a few drops of starch solution, and find that it requires 20.1 c.c. of the iodide solution to give the permanent blue color. Hence 20.1 c.c. = .1270 gramme iodine, or 1 c.c. iodide solution contains .006313 gramme iodine. As the reaction with hydrogen sulphide is $H_2S + 2I = 2HI + S$, it requires 2 equivalents of iodine to decompose 1 equivalent of hydrogen sulphide, and the proportion is 2I : S : : 253.94 : 32.06 : : .006313 : .000797, or 1 c.c. iodine is equal to .000797 gramme sulphur.

The standard solutions once ready, the actual determination of sulphur in a sample is very simple. Pour 50 c.c. of a solution of caustic soda, 1.1 sp. gr., free from sulphur, into the first of the bottles H. The second need not be used, but it is a good plan to keep a caustic potash solution to lead nitrate in it, and attach it after the other, to be certain that no hydrogen sulphide escapes the caustic soda solution. Proceed with the determination as directed on page 55, and when finished wash the contents of the bottle H into a beaker, dilute to 500 c.c., acidulate with hydrochloric acid, add a few drops of starch solution, and titrate with the iodide solution. See exactly how much hydrochloric acid is required to acidulate strongly 50 c.c. of the caustic soda solution, and this amount can be added at once, so that no time need be lost in testing the solution with litmus before titrating.

The Cadmium Method

The use of an ammoniacal cadmium salt to absorb the hydrogen sulphide was first suggested by Morrell (page 58), but instead of weigh-

ing the cadmium sulphide it is now dissolved in hydrochloric acid and the liberated hydrogen sulphide is titrated with iodine. This method is due to E. F. Wood. As this method is now in general use for the rapid determination of sulphur in steel, it seems desirable to describe it more in detail. The reagents required are:—

Starch Solution

(See page 64)

Cadmium Solution

Dissolve 5 grammes of cadmium chloride in 200 c.c. of strong ammonia and dilute to 1 litre.

Iodine Solution

Dissolve 5 to 10 grammes of potassium iodide in as little water as possible, and add 1 gramme of resublimed iodine. When dissolved, dilute to 1 litre.

The Method

Pour 30 to 40 c.c. of the cadmium solution in each of the flasks H and H′ (Fig. 44, page 56), place 5–10 grammes of steel in the flask D and proceed exactly as described on pages 55–57. When the operation is finished, transfer the contents of the flasks H and H′ to a beaker, washing them out with water and filter the precipitated cadmium sulphide on a rapid filter, wash two or three times with water and then place the filter with the precipitate in a litre beaker half full of water. Break up the filter paper with a glass rod and add a few drops of the starch solution. Pour about 100 c.c. of dilute hydrochloric acid, 1 acid to 3 water, into the flask H′ to dissolve any adhering cadmium sulphide, pour it into the flask H, dip the delivery tubes into the acid to clean them, and pour the acid carefully down the side of the beaker containing the filter and precipitate of cadmium sulphide. Run the iodine solution from the burette into the beaker, stirring vigorously. The end reaction is when the faintly pink solution changes to a purplish tint. Subtract from the reading of the burette the amount of iodine solution required to color a blank test made on the same volume of water containing a filter and the amount of hydrochloric acid used in the analysis. The iodine solution should be standardized on a steel containing a known amount of sulphur.

Generally speaking, low carbon steels yield a larger proportion of their sulphur contents as hydrogen sulphide when treated with hydrochloric acid, than high carbon steels, so that the accuracy of the method may be increased by using as a standard a steel of similar constitution to the steel to be analyzed. The blank should of course be subtracted from the reading of the burette before calculating the standard. It usually amounts to 5 to 6 tenths of a c.c.

DETERMINATION OF SILICON

By Solution in Nitric and Hydrochloric Acids

Dissolve 5 grammes of drillings in 40 c.c. nitric acid with the precautions mentioned on page 61; although when silicon *alone* is to be determined, nitric acid of 1.2 sp. gr. may be used, when, in most cases, the solution of the drillings will be more rapid. Remove the cover, evaporate the solution to dryness in the air bath, replace the cover, and raise the temperature of the bath until the ferric nitrate is decomposed. Remove the beaker from the air bath, allow it to cool, add 30 c.c. hydrochloric acid, and heat gradually until all the ferric oxide is dissolved. Remove the cover, and evaporate again to dryness in the air bath, redissolve in 30 c.c. hydrochloric acid, dilute to about 150 c.c., and filter on an ashless filter. Detach any adhering silica from the sides and bottom of the beaker with a "policeman," or with a piece of filter paper, and wash it out with cold water. Wash the filter first with dilute hydrochloric acid, and finally with water. Dry, and ignite in a platinum crucible until all the carbon is burned, weigh the residue in the crucible, moisten it with water, add from 1 to 10 drops sulphuric acid, and enough hydrofluoric acid to dissolve it completely, evaporate to dryness, ignite, and weigh. The difference between the two weights is silica, which contains 46.93 per cent. of silicon. In the absence of hydrofluoric acid, unless the silica is perfectly white, fuse with 5 or 6 times its weight of sodium carbonate, dissolve in water, acidulate with hydrochloric acid, evaporate to dryness (in a platinum or porcelain dish, with the arrangement shown on page 17), redissolve in hydrochloric acid and water, dilute, filter, wash, ignite, and weigh. When the weight of sodium carbonate taken does not exceed 2 or

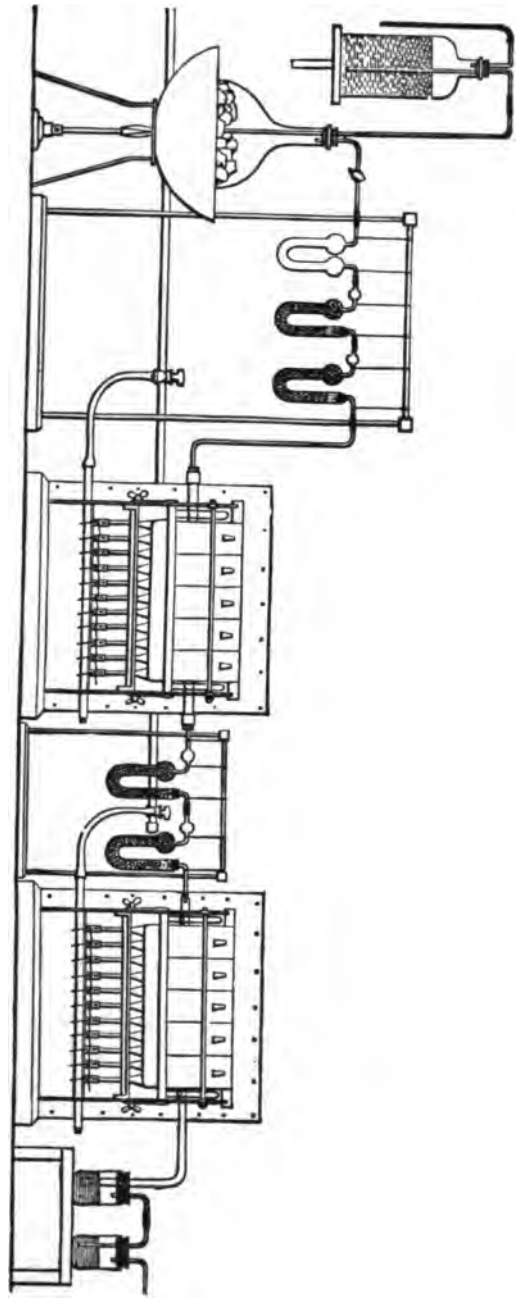


FIG. 46.

3 grammes, allow the crucible to cool after fusion, and then add to it gradually an excess of strong sulphuric acid, heating very slowly, until the mass is quite liquid and fumes of sulphuric anhydride come off. Allow it to cool, dissolve in water, filter, wash well, ignite, and weigh.

By Solution in Nitric and Sulphuric Acids

Drown * has suggested a method which, for pig-irons, has come into very general use, and which is much more rapid than the other method and quite as exact. Treat 1 gramme of borings in a platinum or porcelain dish with 20 c.c. nitric acid, 1.2 sp. gr. When all action has ceased, add 20 c.c. of sulphuric acid (equal parts of acid and water), and evaporate—using the arrangement shown on page 17—until copious fumes of sulphuric anhydride are given off. Allow to cool, and dilute with 150 c.c. water; heat carefully until all the ferric sulphate has dissolved, filter hot,† wash first with dilute hydrochloric acid, 1.1 sp. gr., and then with hot water, ignite, and weigh. Treat the contents of the crucible with sulphuric and hydrofluoric acids, evaporate to dryness, ignite, and weigh again. The difference between the two weights is silica.

By Volatilization in a Current of Chlorine Gas

As almost all steels and irons contain slags of various compositions, it must be understood that the silica obtained by the methods given above is the total silica, comprising any silica that may be present in the admixed slag, as well as that formed from the silicon present in the metal. The volatilization method separates the two. The process suggested by Drown,‡ and worked out independently two years later by Watts,§ is as follows: Fig. 46 shows the general arrangement of the apparatus. The large flask contains strong common manganese dioxide in lumps. The bottle above it contains strong common hydrochloric acid, which runs into the flask through a siphon-tube extending almost to the bottom. The flask stands in a dish containing water, which can be heated by the burner under the tripod. The evolution

* Journal Inst. Min. Engineers, vii. 346.

† Dr. Dudley has shown that upon long standing silica dissolves, and it is therefore advisable to filter the sulphuric acid solution as soon as the ferric sulphate is dissolved.

‡ Jour. Inst. Min. Engineers, viii. 508. § Chem. News, xlv. 279.

tube from the flask has a stopcock, and connects with the three bulb-tubes on the stand, the first containing water, the second pumice-stone, and the third pumice saturated with strong sulphuric acid. The outlet-tube from the latter leads into the porcelain or glass tube in the furnace. This tube contains small lumps of charcoal or gas carbon, kept in position by loosely fitting plugs of asbestos, and occupying about 8 inches (200 mm.) in the middle of the tube. The outlet tube from this connects with the drying tubes on the second stand, which contain pumice moistened with strong sulphuric acid. The outlet from the second drying-tube connects with the glass combustion-tube, which leads through the second furnace, and is bent at a right angle where it is connected with the large tubes, half filled with water. The apparatus being in order,* start a slow current of chlorine through the apparatus by blowing hydrochloric acid from the bottle into the flask and filling the dish in which the latter stands with water. Light a low light under the dish, and open the stopcock wide enough to allow a very slow current to bubble through the bulbs. Light the burners of the first furnace so that the tube is heated to dull redness. When the apparatus is full of chlorine, place 1 gramme of pig-iron, or 3 grammes of steel, in a porcelain boat about 3 inches long, distributing the drillings evenly along the bottom of the boat. Remove the stopper at the rear end of the second tube and insert the boat to about the center. Replace the stopper, and continue the current of chlorine in the cold for ten or fifteen minutes to make sure that no oxygen remains in the tube, then light the burner under the forward end of the boat. The heat must be just sufficient to volatilize the ferric chloride, which should condense in the cooler part of the tube, and the current of gas should be slow enough to prevent any ferric chloride from being carried forward into the water-tubes or any loss of carbon from the boat. When the fumes of ferric chloride begin to come off more slowly, light the next burner, and continue until all the burners under the boat are lighted, maintaining the heat until the fumes of ferric chloride cease. The tube for the entire length occupied by the boat should be at a dull red

* All the stoppers used should be of rubber coated with paraffine on the ends, or of asbestos, and where glass tubes are joined together with rubber the ends of the glass tubes should be brought into close contact.

heat. Should the condensed ferric chloride at any time choke the tube so as to prevent the passage of the gas, heat that part of the tube gently with a spirit lamp, so as to drive the ferric chloride a little farther along the tube. When the fumes of ferric chloride are no longer given off from the boat, the operation may be considered finished. Turn out the lights under the tube containing the boat, remove the stopper, and draw out the boat, which now contains the carbon, the slag, and the greater part of the manganese (as chloride) which were contained in the iron and steel. This residue may be used for the determination of the carbon or the slag, as will be shown farther on. If another determination is to be made, another tube may be substituted for the one which contained the boat, and the analysis carried out in the manner described above. If not, put out all the lights, close the stop-cock, and withdraw the combustion-tube with the water-tubes. Remove the stoppers from the latter, and pour the contents of these tubes into a platinum dish containing a small amount of an aqueous solution of sulphurous acid, to prevent the chlorine in the solutions from acting on the platinum. Rinse the tubes into the dish, and if any silica has separated and adheres to the water-tubes or to the end of the combustion-tube, loosen it with a "policeman" and wash it into the dish. Add 5 c.c. strong sulphuric acid, evaporate to dryness, and heat until fumes of sulphuric anhydride are given off. Allow the dish to cool, add 100 c.c. cold water, and filter the silica on a small ashless filter. Burn and weigh as silica. Calculate to Silicon. The filtrate from the silica will contain any titanic acid which may have been in the metal and which can be determined, as will be shown farther on. Silicon and titanium are volatilized as chlorides, under the conditions shown above, and decomposed by water thus: $SiCl_4 + 2H_2O = 4HCl + SiO_2$ and $TiCl_4 + 2H_2O = 4HCl + TiO_2$.

Rapid Method for Determination of Silicon. (S. Alfred Ford*)

At the Edgar Thomson Steel Works the molten pig-metal is taken directly from the furnaces to the converters, and it is generally necessary

* Prepared by Mr. Ford for this volume.

to determine the amount of silicon in the pig-iron as a guide in blowing the metal. To get the sample for analysis, a small ladle is dipped into the iron as it runs from the furnace, and a small quantity of molten iron is taken. The ladle is then held about three feet above a bucket of water, and the molten metal dropped into the water, at the same time giving the ladle a circular motion over the bucket. This will cause the iron to form in globules, more or less round according to the amount of silicon contained in the iron. Thus, with iron which contains 2 per cent. of silicon or more, the globules will be almost perfectly round, concave on the upper surface and generally from ¼ inch (6 mm.) to ⅜ inch (9 mm.) in diameter; while if the iron be low in silicon, the shot or drops will be very small, flat, and irregular in shape, and if the iron be very low in silicon, as is the case with spiegel and ferro-manganese, the shot will be elongated and have tails sometimes ¼ inch (6 mm.) in length. In fact, a close observer can soon judge very closely as to the amount of silicon from the condition of these shot or drops. The next step in the process is to take the shot from the bucket and place them for a minute in the ladle which has been used to dip up the molten iron. The ladle, being hot, will dry the shot almost instantly. The shot are then placed in a large steel mortar (Fig. 5, page 14) and crushed. The crushed shot are then sifted with a fine sieve, and .5 gramme of the fine siftings are placed in a platinum evaporating-dish, 10 c.c. hydrochloric acid, 1.2 sp. gr., are then added, and the dish covered with a watch-glass. The dish is then placed over a light, and the iron dissolved; as soon as solution takes place, which requires about one minute, as the particles of iron are so small, the watch-glass is removed and the solution evaporated to dryness as rapidly as possible over a naked light; as soon as dry, not even waiting for the dish to cool, dilute hydrochloric acid is dropped on the ferric chloride, and as soon as all the ferric oxide (which may have been formed by the decomposition of the chloride) is dissolved, water is added. The contents of the dish are then poured on a filter, to which is attached a pump, filtered, and washed. The filter and its contents are then placed in a weighed platinum crucible, placed over a blast-lamp; as soon as the filter-paper is burned off, the crucible is turned on its side, the lid removed, and a small jet of oxygen is driven very gently into the crucible. As soon as what little carbon there is in

the precipitate is burned off, the crucible is cooled and weighed, and the amount of silicon calculated from the weight of the silica in the crucible.

By this method the amount of silicon in a pig-iron can be determined in twelve minutes from the time the ladle is put into the molten iron, and it gives results close enough for practical purposes.

DETERMINATION OF SLAG AND OXIDES

A certain amount of slag and oxide of iron is always present in puddled iron as a mechanical admixture. It is also found, as a general thing, in basic steel, and the presence of slag in steel made by the acid process, as well as in pig-iron, is not unusual. The easiest method for the determination of these substances is by solution in iodine, as suggested by Eggertz.

By Solution in Iodine

Place 5 grammes of borings free from lumps in a 250 c.c beaker. Stand the beaker, carefully covered with a watch-glass, in a dish filled with scraped ice or snow, so that the bottom and sides of the beaker half-way up shall be in contact with it. Pour over the iron in the beaker 25 c.c. of ice-cold boiled water, and stir until all the air in the borings has escaped. Add gradually from 28 to 30 grammes of resublimed iodine,* stirring occasionally, until all the iodine has dissolved. Keep the beaker constantly surrounded by ice, and add the iodine slowly enough to prevent any rise in the temperature of the solution. Stir the solution frequently until the iron is perfectly dissolved, which will take several hours; then add 100 c.c. cold boiled water, allow the insoluble matter to settle, and decant the supernatant fluid on a small ashless filter. Wash the insoluble matter several times, by decantation, with cold water, then add to it a little water, with a few drops of hydrochloric acid, and observe whether any hydrogen is disengaged. If none can be perceived, the metallic iron may be considered entirely dissolved; but if gas is given off, the opposite is the case. In either event, quickly decant the acidulated water on the filter, and if any metallic iron remains, add a very little water and some iodine to dissolve the iron entirely. Then transfer the insoluble matter, consisting of

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* Page 37.

graphite, carbonaceous matter, slag, iron oxide, and some silica, to the filter, wash the filter once with very dilute hydrochloric acid (1 acid to 20 water), and finally with cold water, until the filtrate is free from iron. Unfold the filter, and with a fine jet wash off the insoluble matter into a small platinum or silver dish. Evaporate almost to dryness, add 50 c.c. solution of caustic potash, sp. gr. 1.1, and boil five or ten minutes. Decant the liquid on a very small ashless filter, repeat the boiling with fresh caustic potash, transfer the insoluble matter to the filter, and wash well with hot water. Wash once with dilute hydrochloric acid (1 acid to 20 water), and finally with hot water, until the filtrate gives no precipitate with a solution of silver nitrate. Dry, ignite, and weigh as Slag and Iron Oxide.

Instead of using iodine directly for the solution of the iron, a solution of iodine in iron iodide, as suggested by Eggertz,* may be used to great advantage, as it affords a ready method for getting rid of the impurities usually present in resublimed iodine. Treat 5 grammes of iron (as free as possible from silicon) with 25 grammes of iodine, and when the solution is complete, add 30 grammes more of iodine, which will dissolve in the iron iodide in a few minutes. Dilute to 50 c.c. with cold boiled water and filter through a washed filter. Add the filtrate at once to 5 grammes of the weighed sample, and, after solution is complete, proceed as directed above.

By Volatilization in a Current of Chlorine Gas

Proceed exactly as in the method for the determination of silicon (pages 70 *et seq.*) until the boat is withdrawn from the combustion-tube. Wash the contents of the boat into a small beaker with a jet of cold water, and filter on a small ashless filter. The water dissolves any soluble metallic chlorides which are not volatile at a low red heat, and the insoluble matter in the filter consists of slag and carbon. Burn off the carbon and weigh the residue as Slag and Oxides. Or, if the carbon has been determined by another operation, filter the carbon and slag on a counterpoised filter † or on a Gooch crucible, dry at 100° C., and weigh as Carbon, Slag, and Oxides; by subtracting the weight of the carbon the difference is Slag and Oxides.

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* Jern-Kontorets Annaler, 1881, p. 301, and Chem. News, xliv. 173.

† See page 26.

DETERMINATION OF PHOSPHORUS

For the determination of phosphorus in iron and steel but two methods are in general use, either of which, properly carried out, will give extremely accurate results. Some chemists prefer one method, some the other, while a combination of the two is sometimes used. The two general methods are known respectively as the *Acetate Method* and the *Molybdate Method.* There are innumerable variations in the details, especially of the latter method, but any departure from what might be termed the standard instructions should never be attempted by any but a very experienced analyst.

The Acetate Method

The essential parts of this method were suggested by Fresenius,* the changes and improvements in detail being the work of many chemists.†

Treat 5 grammes of drillings in a 600 c.c. beaker with 80 c.c. nitric acid (1.2 sp. gr.), and, when violent action has ceased, add 10 c.c. strong hydrochloric acid. Evaporate the solution to dryness in the air-bath, replace the cover, and heat until the ferric nitrate is nearly all decomposed. Cool, add 30 c.c. hydrochloric acid, heat gradually until the iron oxide is dissolved, and evaporate to dryness again in the air-bath. Cool, dissolve in 30 c.c. hydrochloric acid, dilute, and, in steels or puddled iron, when silicon is to be determined, filter, and treat the insoluble matter as directed for the determination of silicon, on page 68.

In the case of pig-irons which may contain titanium, filter, and keep the residue of graphite, silica, etc., for treatment, as directed farther on, " when titanium is present."

In the case of steels, when silicon is not to be determined in this portion, the solution need not be filtered at all, but may be diluted at once to about 250 c.c.

In any case, heat the filtered or unfiltered hydrochloric acid solution nearly to boiling, remove the beaker from the light, and add gradually from a small beaker a mixture of 10 c.c. acid ammonium sulphite ‡ and 20 c.c.

* Jour. für Pr. Ch., xlv. 258.

† Tenth Census of the U. S., vol. xv. " Iron Ores of the U. S.," p. 523.

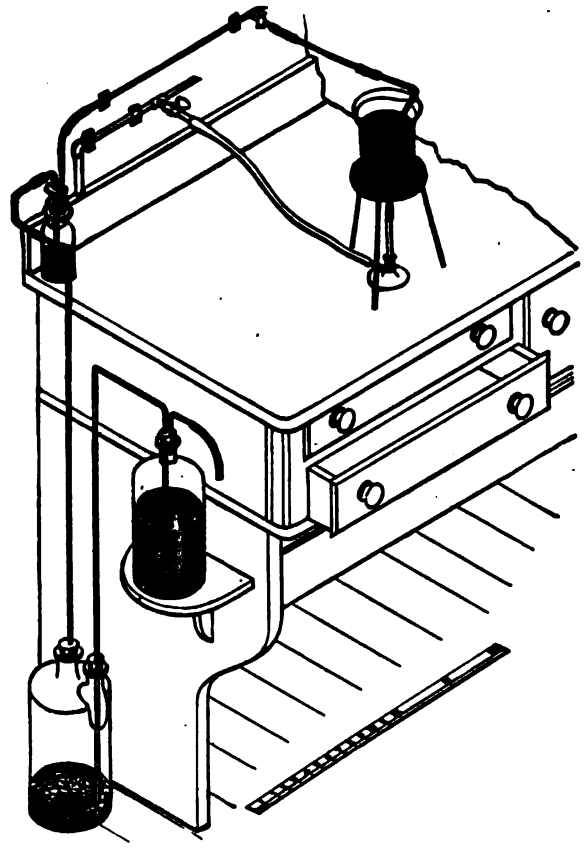
‡ See page 39.

ammonia, stirring constantly. The precipitate, which forms at first, redissolves, and when all but about 2 or 3 c.c. of the acid ammonium sulphite solution has been added, replace the beaker over the light. If at any time while adding the acid ammonium sulphite solution the precipitate formed will not redissolve even after vigorous stirring, add a few drops of hydrochloric acid, and, when the solution clears, continue the addition, very slowly, of the acid ammonium sulphite. After replacing the beaker on the light, add to the solution (which should smell quite strongly of sulphurous anhydride) ammonia, drop by drop, until the solution is quite decolorized, and until finally a *slight* greenish precipitate remains undissolved even after vigorous stirring. Now add the remaining 2 or 3 c.c. of the acid ammonium sulphite solution, which should throw down a white precipitate, which usually redissolves, leaving the solution quite clear and almost perfectly decolorized. Should any precipitate remain undissolved, however, add hydrochloric acid, drop by drop, until the solution clears, when it should smell perceptibly of sulphurous anhydride. If the reagents are used in exactly the proportions indicated, the reactions will take place as described, and the operations will be readily and quickly carried out. If the solution of acid ammonium sulphite is weaker than it should be, of course the ferric chloride will not be reduced, and the solution, at the end of the operation described above, will not be decolorized and will not smell of sulphurous anhydride. In this case add more acid ammonium sulphite (without the addition of ammonia) until the solution smells strongly of sulphurous anhydride, then add ammonia until the slight permanent precipitate appears, and redissolves it in as few drops of hydrochloric acid as possible. The solution being now very nearly neutral, the iron in the ferrous condition, and an excess of sulphurous acid present, add to the solution 5 c.c. of hydrochloric acid to make it decidedly acid and to insure the complete decomposition of any excess of the acid ammonium sulphite which may be present. Boil the solution,* while a stream of carbonic acid passes through it, until every trace of sulphurous anhydride is expelled, then pass a current of hydrogen sulphide through it for about fifteen minutes to precipitate any arsenic which may be present, and finally

* By passing a current of carbonic acid through the boiling solution the sulphurous anhydride is soon expelled, and the operation requires no watching.

allow the solution to stand in a warm place until the smell of hydrogen sulphide has disappeared, or better, pass a current of carbonic acid through the solution, which will expel the hydrogen sulphide in a few minutes. The arrangement, Fig. 47, is convenient for this purpose. Filter from any arsenious sulphide, cuprous sulphide, sulphur, etc., into a 600 c.c.

FIG. 47.



beaker, wash with cold water, and to the filtrate add a few drops of bromine-water, or of a solution of ferric chloride, and cool it by placing the beaker in cold water. To the cold solution add ammonia from a small beaker very slowly, and finally, drop by drop, with constant stirring. The green precipitate of ferrous hydrate which forms at first is dissolved

by stirring, leaving the solution perfectly clear, but subsequently, although the green precipitate dissolves, a whitish one remains, and the next drop of ammonia increases the whitish precipitate or gives it a reddish tint, and finally the greenish precipitate remains undissolved even after vigorous stirring, and another drop of ammonia makes the whole precipitate appear green. If before this occurs the precipitate does not appear decidedly red in color, dissolve the green precipitate by a drop or two of hydrochloric acid, and add a little bromine-water or ferric chloride solution (1 or 2 c.c.), then add ammonia as before, and repeat this until the reddish precipitate is obtained, and then the green coloration as described above. Dissolve this green precipitate in a very few drops of acetic acid (sp. gr. 1.04), when the precipitate remaining will be quite red in color, then add about 1 c.c. of acetic acid, and dilute the solution with boiling water, so that the beaker may be about four-fifths full. Heat to boiling, and when the solution has boiled one minute, lower the light, filter as rapidly as possible through a 5½-inch (140-mm.) filter, and wash once with hot water. The filtrate should run through clear, but in a few minutes it will appear cloudy by the precipitation of the ferric oxide, which has been formed by the exposure of the filtered solution to the air. The points to be observed are the red color of the precipitate and the clearness of the solution when it first runs through. Ferric phosphate being white, the red color of the precipitate shows that enough ferric salt was present in the solution to form ferric phosphate with all the phosphoric acid, and enough more to color the ferric phosphate red with the excess of ferric oxide.

When the precipitate has drained quite dry, pour about 15 c.c. of hydrochloric acid into the beaker in which the precipitation was made, warm it slightly so that the acid may condense on the sides and dissolve any adhering oxide, wash off the cover into the beaker, add about 10 c.c. of bromine-water, pour this on the filter containing the precipitate, allowing it to run around the edge of the filter, and let the solution run into a 250 c.c. beaker. Wash the beaker once or twice, and then wash the filter well with hot water. If the acid in the beaker is not sufficient to dissolve the precipitate completely, drop a little strong acid around the edge of the filter before washing it with hot water. The scaly film of difficultly soluble oxide which sometimes forms on boiling the acetate

precipitate is caused by the presence of too much ammonium acetate, but when the instructions given above are carefully carried out it never appears. Evaporate the solution in the small beaker nearly to dryness to get rid of the excess of hydrochloric acid, add to it a filtered solution of 5 or 10 grammes of citric acid (according to the size of the precipitate of ferric oxide, etc.) dissolved in from 10 to 20 c.c. of water, then from 5 to 10 c.c. of magnesia-mixture and enough ammonia to make the solution faintly alkaline. Stand the beaker in cold water, and when the solution is perfectly cold, add to it one-half its volume of strong ammonia and stir it well. When the precipitate of ammonium-magnesium orthophosphate has begun to form, stop stirring, and allow it to stand in cold water for ten or fifteen minutes, then stir vigorously several times, at intervals of a few minutes, and allow it to stand overnight. Filter on a small ashless filter, and wash with a mixture of 2 parts of water and 1 part of ammonia containing 2.5 grammes of ammonium nitrate to 100 c.c.

Dry the filter and precipitate, and ignite them at a very low temperature at first so as to carbonize the filter without decomposing the precipitate, which may then readily be broken up with a platinum wire. Raise the heat gradually, and finally ignite at the highest temperature of the Bunsen burner. When the precipitate is perfectly white, cool and weigh. Then fill the crucible half full of hot water, add from 5 to 20 drops of hydrochloric acid, and heat until the precipitate has dissolved. Filter off on another small, ashless filter any silica or ferric oxide that may remain, ignite, and weigh. The difference between the two weights is the weight of magnesium pyrophosphate, which, multiplied by 0.27838, gives the weight of phosphorus.

When Titanium is Present

When a solution of ferric chloride containing titanic and phosphoric acids is evaporated to dryness, a compound of titanic acid, phosphoric acid, and ferric oxide is formed, completely insoluble in dilute hydrochloric acid.*

Iron ores and pig-irons containing titanic acid require, therefore, a somewhat different method of treatment from that given above.

* Published in Report on Methods employed in the Analysis of the "Iron Ores," Tenth Census U. S., xv. 512. I first noted this fact in 1878.

Dry and ignite the residue of graphite, silica, etc., from the solution of the pig-iron, so as to burn off all the carbon. Moisten this residue with cold water, add from 5 to 10 drops of sulphuric acid and enough hydrofluoric acid to dissolve the silica, and evaporate until fumes of sulphuric anhydride are given off. While this is going on, proceed with the deoxidation of the filtrate as described above, but when the sulphurous acid has been driven off do not pass hydrogen sulphide through the solution, but cool it, and proceed with the acetate precipitation. Instead of dissolving the precipitate, after washing it as described above, dry the filter and precipitate in the funnel, being careful not to heat it so as to scorch the filter. Clean out any of the precipitate which may have adhered to the sides of the beaker in which the precipitation was made, by wiping it with filter-paper, and dry this paper with the filter and precipitate.

When the precipitate is quite dry, transfer to a small porcelain mortar. The precipitate may readily be detached from the filter by rubbing the sides of the latter together over a large piece of white, glazed paper, so that any little particles that fall out may be seen. Roll up the filter with the bits of paper which were used to wipe out the beaker, wrap a piece of platinum wire around it, burn it on the lid of the crucible in which the graphite residue was treated, and transfer the ash to the mortar. Grind the precipitate and ash with from 3 to 5 grammes of sodium carbonate and a little sodium nitrate, and transfer it to the crucible containing the residue which was treated by hydrofluoric and sulphuric acids. Clean the mortar and pestle by grinding a little more sodium carbonate, and add this to the other portion in the crucible. Fuse the whole for half an hour or more, cool, dissolve the fused mass in hot water, filter from the insoluble ferric oxide, etc.,* acidulate the filtrate with hydrochloric acid, add a few drops of acid ammonium sulphite, boil off all smell of sulphurous acid, and pass hydrogen sulphide through the hot solution to precipitate any arsenic that may be present. Pass a current of carbonic acid through the solution to expel the excess of hydrogen sulphide, filter off the arsenious sulphide, and to the filtrate add a

* This ferric oxide, etc., contains all the titanium that was in the pig-iron as titanate of soda, and must be kept for the estimation of that element when it is to be determined.

sufficient amount of ferric chloride solution to combine with all the phosphoric acid as ferric phosphate and leave a slight excess. Add a slight excess of ammonia, which should throw down a red precipitate, while the solution is alkaline to test-paper; then add acetic acid to slightly acid reaction, boil, filter off the ferric phosphate and ferric oxide, and wash with hot water. Dissolve the precipitate in hydrochloric acid, allow the solution to run into a small beaker, evaporate until the solution is syrupy, add citric acid and magnesia-mixture, and precipitate the ammonium-magnesium orthophosphate as described above. Unless the amount of phosphorus is very small, a second fusion of the insoluble residue of ferric oxide, etc., is necessary. The two filtrates can then be added together, acidulated with hydrochloric acid, and the remainder of the process carried out as directed above. To avoid the fusion of the acetate precipitate with sodium carbonate, which is always troublesome, the method for the determination of phosphorus may be modified (in many cases with advantage, and generally when titanium is not to be estimated) as follows:

After filtering off the insoluble matter,—graphite, silica, etc.,—ignite it, burn off the graphite, and treat the residue with hydrofluoric and sulphuric acids, evaporate down until the excess of sulphuric acid is driven off and fuse with sodium carbonate. Treat the fused mass with water, and filter. Acidulate the filtrate with hydrochloric acid, and add it to the main solution, which has been deoxidized in the meantime with acid ammonium sulphite. Expel the last traces of sulphurous acid from the united filtrates by boiling and passing a current of carbonic acid through the solution, as previously directed. If the solution remains clear, pass hydrogen sulphide through it, and filter off the precipitated sulphides. Cool the solution, and make the acetate precipitation as directed on page 76. The only danger to be apprehended now is the tendency of titanic acid to separate out and carry phosphoric acid with it when in the evaporation of the hydrochloric acid solution of the acetate precipitate the liquid becomes concentrated. To avoid this, the evaporation must be watched very carefully, and citric acid added as soon as the titanic acid begins to separate. Then, if the separation has not proceeded too far, the phosphoric acid may be precipitated in the

usual way. If, however, the separations of titanic acid is not checked in time, proceed with the evaporation as directed on page 79, add 5 c.c. strong hydrochloric acid, and warm gently. The solution will nearly always clear, but if it does not, add citric acid and a slight excess of ammonia, and filter. Stand the filtrate aside, burn off and fuse the precipitate with sodium carbonate, dissolve in water, filter, acidulate the filtrate with hydrochloric acid, add a little ferric chloride solution, a slight excess of ammonia, and acidulate with acetic acid. Boil, filter off the precipitate of ferric phosphate and oxide, dissolve in a little hydrochloric acid, allow the solution to run into a small beaker, evaporate down, and add it to the ammoniacal filtrate from the separated titanic acid obtained above. Add excess of magnesia-mixture, and precipitate the phosphoric acid in the usual way. When the solution becomes cloudy after deoxidation with acid ammonium sulphite, and remains so after acidulating with hydrochloric acid, proceed as directed above, but dry, and ignite the filter containing the precipitate by hydrogen sulphide and that on which the acetate precipitate was filtered, fuse with sodium carbonate, treat with water, filter, acidulate with hydrochloric acid, pass hydrogen sulphide through the solution, filter, add a little ferric chloride solution, and precipitate by ammonia and acetic acid. Add the solution of this precipitate, after filtering it off, to the solution of the main acetate precipitate, and proceed as before.

Instead of adding citric acid and magnesia-mixture to the solution of the acetate precipitate, Fresenius,* and afterwards Spiller,† advised the method of adding citric acid, excess of ammonia, and ammonium sulphide, filtering off the precipitated ferric sulphide, and, after evaporating to small bulk, adding magnesia-mixture and ammonia. When the bulk of the iron precipitate is not too great, this is quite unnecessary, for many determinations have shown that with an excess of magnesia-mixture, ammonium-magnesium orthophosphate is absolutely insoluble in both ferric-ammonium citrate and ammonium-aluminum citrate.

The precipitate is also insoluble in ammonia-water (1 part of ammonia to 2 parts of water).

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* Jour. für Pr. Chem., xlv. 258. † Jour. Chem. Soc. (2), i. 148.

The Molybdate Method

Svanberg and Struve* first discovered the reaction on which this method is based, and Sommenschein† first used it quantitatively. Dissolve 5 grammes of drillings in a 600 c.c. beaker, in 80 c.c. nitric acid (1.2 sp. gr.). Evaporate to dryness in the air-bath, replace the cover, and heat for one hour at a temperature of about 200° C. in order to decompose all the carbonaceous matter, otherwise the precipitation of the phospho-molybdate will be incomplete. Allow the breaker to cool, dissolve the precipitate in 30 c.c. hydrochloric acid, evaporate to dryness to render the silica insoluble, redissolve in 30 c.c. hydrochloric acid, and evaporate carefully until the excess of hydrochloric acid is driven off. Add 30 c.c. nitric acid and evaporate nearly dry, add nitric acid again and evaporate to drive off all the hydrochloric acid, add from 50 to 100 c.c. molybdate solution,‡ heat it to 40° C. in a water-bath carefully kept at this temperature, and allow it to stand in the bath for about four hours. Filter on a small, washed filter, and wash thoroughly with dilute molybdate solution (1 part of solution to 1 part of water) until a drop of the filtrate gives no reaction for iron with potassium ferrocyanide. Stand the filtrate aside in a warm place to see whether any further precipitation of ammonium phospho-molybdate takes place; if it does, it must be filtered off and treated like the main precipitate. Pour 2 or 3 c.c. strong ammonia on the precipitate, stir it up with a fine jet of hot water, and allow the solution to run into the flask or beaker in which the precipitation of phospho-molybdate was made. When it has all run through the filter, replace the flask or beaker by a small beaker of a little over 100 c.c. capacity, remove any phospho-molybdate that may have adhered to the sides of the original flask or beaker, by means of the ammoniacal filtrate, and then pour this back on the filter and allow it to run through into the small beaker. Wash out the beaker or flask with hot water and pour it on the filter with the addition of a little more ammonia. Unless the precipitate of phospho-molybdate is very large, this amount of ammonia should dissolve it, and a very little more washing should be sufficient. If the precipitate is very large, it may be necessary to use more ammonia and more wash-water, but

* Jour. für Pr. Chem., xliv. 291. † Ibid., liii. 339.

‡ See page 54.

under all circumstances the amount of ammonia and of wash-water should be as small as is consistent with perfect solution of the precipitate and thorough washing of the beaker and filter. When the precipitate is small, the filtrate and washings should amount to about 25 c.c. Neutralize the solution with strong hydrochloric acid; if the yellow phospho-molybdate begins to precipitate, add ammonia until it redissolves, and if there should remain a flocculent white precipitate, probably silica, after the solution is quite alkaline, filter it off. Then to the cold alkaline liquid add, very slowly, 10 c.c. magnesia-mixture, stirring constantly, and after the magnesia-mixture is all in, add one-third the volume of the solution of strong ammonia and stir vigorously. It is well to stand the beaker in cold water and stir the solution several times after the precipitate has begun to crystallize out. After standing about four hours, it may be filtered off on a very small ashless filter and washed with dilute ammonia-water (1 part ammonia, 0.9 sp. gr., to 2 parts water) containing 2.5 grammes ammonium nitrate to the 100 c.c. Dry, ignite very carefully to burn off the carbonaceous matter, and finally heat for ten minutes over the blast-lamp to volatilize any molybdic acid that may have been precipitated with the ammonium-magnesium orthophosphate, cool, and weigh. Fill the crucible half full of hot water, add from 5 to 20 drops hydrochloric acid, and heat for a few minutes to dissolve the magnesium pyrophosphate. Pour the contents of the crucible on a small ashless filter, wash, ignite, and weigh the small residue that may remain undissolved. The difference between the two weights is the weight of magnesium pyrophosphate, which contains 27.874 per cent. phosphorus.

Many chemists, following Eggertz,* prefer to weigh the yellow phospho-molybdate direct instead of dissolving it and precipitating as ammonium-magnesium orthophosphate. In this event take 1 gramme of the drillings and proceed exactly as directed above, but use only about one-third the amount of nitric and hydrochloric acids for the solution. Before adding the molybdate solution, the volume of the filtrate from the silica should amount to only about 25 c.c. Add 50 c.c. of the molybdate solution, allow it to stand four hours at a temperature of 40° C., and filter off the precipitated phospho-molybdate on a Gooch crucible; wash first with

* Jour. Für Pr. Chem., lxxix, 496.

dilute molybdate solution, and finally with water containing 1 per cent. of nitric acid, dry in an air-bath heated at 120° C., and weigh as ammonium phospho-molybdate, containing 1.63 per cent. of phosphorus. In the absence of a Gooch crucible, use counterpoised filters * for weighing the phospho-molybdate. The points of special importance are:

First, the necessity for destroying all the carbonaceous matter by heating the nitric acid solution, after evaporation, to a sufficiently high temperature to effect this with certainty.

Second, the avoidance of the presence of hydrochloric acid in the final solution before precipitating by molybdate solution.

Third, when the phospho-molybdate is weighed directly, the necessity for rendering the silica insoluble.

Fourth, the danger of heating the solution above 40° C. after adding the molybdate solution, as arsenic, when present, precipitates with the phosphorus if the solution is heated to a higher temperature.

Fifth, the danger of causing a precipitation of molybdic acid with the phospho-molybdate by heating the solution to a temperature approximating 100° C.

The Combination Method

Riley † was the first to suggest the precipitation of phosphorus as phospho-molybdate, preceded by a separation of the phosphoric acid from the mass of the ferric chloride by deoxidation and precipitation by the acetate method. This method was worked out afterwards by A. Wendel, of the Albany and Rensselaer Steel Company, S. Peters, of the Burden Iron Company, and J. L. Smith.‡

Proceed as directed for the determination of phosphorus by the *Acetate Method,* using 1 gramme of borings and proportional amounts of reagents until having dissolved the acetate precipitate in hydrochloric acid, evaporate to dryness, redissolve in a very little nitric acid, dilute to 20 c.c. wth water, add a slight excess of ammonia, redissolve the precipitated ferric oxide in nitric acid, and add 30 c.c. molybdate solution. Heat to 40° C. for an hour, filter, wash with water containing 1 per cent. of nitric acid, dry, and weigh.

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* See page 26.

† Jour. Chem. Soc., 1878, i. 104.

‡ Chem. News, xlv. 195.

When Titanium Is Present

When determining phosphorus in pig-irons containing titanium, burn off the residue of carbon silica, etc., treat it with hydrofluoric and sulphuric acids, evaporate, and heat until the greater part of the sulphuric acid is driven off. Fuse with 2 or 3 grammes of sodium carbonate, dissolve in water, filter, acidulate the filtrate with nitric acid, add 50 c.c. molybdate solution, and heat to 40° C. for four hours. Filter, wash, and add this precipitate to the one obtained in the filtrate from the carbon, silica, etc. If any slight insoluble matter should remain on the filter upon dissolving in ammonia the phospho-molybdate obtained in the filtrate from the carbon, silica, etc., burn it, fuse it with sodium carbonate, and test it also for phosphorus.

The composition of the dried ammonium phospho-molybdate seems to vary very much, the percentage of phosphorus in it being given by various authorities from 1.27 to 1.75. It seems to depend upon various circumstances, such as the presence or absence of hydrochloric acid in the solution, the degree of acidity, the temperature at which the precipitation is effected, the length of time the solution stands before the precipitate is filtered off, the size of the precipitate, the state of concentration of the solution, and even the amounts of the iron and ammonium salts present.

This fact must be borne in mind when the phosphorus is determined by direct weighing of the phospho-molybdate, and every effort must be used to effect the precipitations always under as nearly as possible the same conditions.

RAPID METHODS

Volumetric Method *

Reduction by Zinc and Titration by Permanganate Solution

This method gives an indirect determination of phosphorus by means of the estimation of the molybdic acid in the ammonium phospho-molybdate,

* This method is the one prepared by the sub-committee on Methods of the International Steel Standards Committee of the United States. It is by far the best method known, and the results obtained by it are exceedingly accurate when the details are carefully observed. The sub-committee consists of W. P. Barba, A. A. Blair, T. M. Drown, C. B. Dudley (chairman), and P. W. Shimer.

in which form the phosphorus is precipitated. The molybdic acid is reduced to a lower state of oxidation by the reducing action of zinc and sulphuric acid, and the reduced oxide is titrated with a standardized permanganate solution, molybdic acid being again formed by the reaction.

FIG. 48.

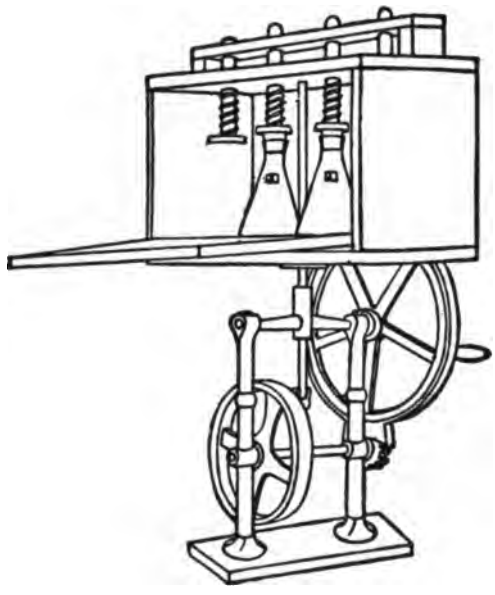


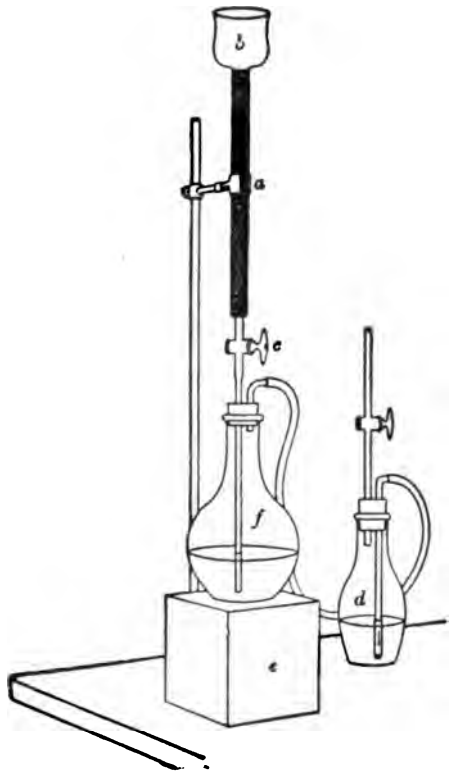
Fig. 48 shows a form of shaking-machine for shaking four flasks at once. The construction and method of use are apparent from the sketch.

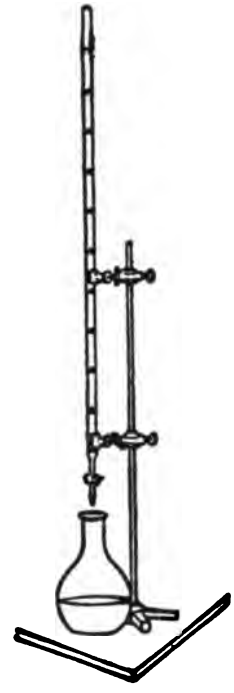
Fig. 49 shows a form of reductor which is most convenient and efficient. The tube *a* is 0.018 m. inside diameter and 0.300 m. long. The small tube below the contraction with the stopcock *c* is 0.006 m. in inside diameter and 0.300 m. long below the stopcock. The tube is filled by placing at the point of contraction a flat piece of fine platinum gauze. On top of this is placed a plug of glass wool, about 8 mm. thick, and then asbestos, previously treated with concentrated hydrochloric acid, thoroughly washed, ignited, and diffused in water, is poured into the reductor tube until it forms a coating on top of the glass wool not over 1 mm. thick. This makes a filter which prevents very small pieces of zinc or other materials from being carried through. It is necessary to clean and refill the tube from time to time, as the filter after some use becomes clogged and the liquid passes too slowly. The tube is filled, as shown in the cut, with granulated amalgamated zinc. The reductor tube is fixed at such a height that when the block is removed from under the flask *f*, the latter may readily be detached from the tube and removed without disturbing the apparatus.

Fig. 49*a* shows the burette arranged for running the potassium perman-

ganate directly into the flask, and needs no explanation. It should be carefully calibrated.

Fig. 49. Fig. 49*a*.





The various beakers, flasks, graduates, etc., required by this method need no special comment.

Reagents

Nitric Acid.—Nitric acid of 1.135 sp. gr., made by mixing C. P. nitric acid (1.42 sp. gr.) with about three parts of distilled water.

Strong Sulphuric Acid.—The C. P. material of 1.84 sp. gr.

Dilute Sulphuric Acid.—Sulphuric acid 2½ per cent., by volume, made by diluting 25 c.c. of concentrated C. P. sulphuric acid to 1 litre with distilled water.

Strong Ammonia.—The C. P. material of 0.90 sp. gr.

Dilute Ammonia (0.96) sp. gr.).—Made by mixing concentrated C. P. ammonia-water of 0.90 sp. gr. with about one and a half times its volume of distilled water.

Strong Solution of Potassium Permanganate, for oxidizing the phosphorus and carbonaceous matter in the nitric acid solution of a steel. Made by dissolving from 12.5 to 15 grammes of crystallized potassium permanganate in 1 litre of distilled water and filtering through asbestos.

Standard Solution of Potassium Permanganate, for titrating the reduced solutions of ammonium phospho-molybdate. Made by dissolving 2 grammes of crystallized potassium permanganate in 1 litre of distilled water and filtering through asbestos. This solution is standardized as follows. Weigh accurately one portion of .25 and one of .3 gramme of Sorenson's sodium oxalate * and transfer carefully to 300 c.c. Erlenmeyer flasks. Add to each 150 c.c. boiling distilled water and 20 c.c. of sulphuric acid, 1 part strong acid 1.84 sp. gr., and 3 parts water which has been boiled to get rid of ozone which is always given off when strong sulphuric acid is diluted. Add to the hot solution in the flask a drop or two of permanganate from the burette. The color of the permanganate remains for a few moments and when it has disappeared add a few more drops, the color from which disappears much more quickly, after which the permanganate may be added quite rapidly, the color disappearing instantly. When about 54.7 c.c. have been added to the .25 gramme portion or 65.6 c.c. to .3 gramme portion, heat the solution in the flask almost to boiling and then add the permanganate drop by drop until a faint permanent pink color is obtained. The reaction is

$Na_2C_2O_4 + H_2SO_4 = Na_2SO_4 + H_2C_2O_4$ and $5H_2C_2O_4 + 3H_2SO_4 + 2KMnO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$.

Then as, $10F_2SO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$, one molecule of Sodium Oxalate is equivalent in reducing power to two molecules of ferrous iron, and one gramme of the oxalate

* Sodium oxalate C. P. is now furnished by the Bureau of Standards, Washington, D. C. The investigation by R. S. McBride, Journal American Chemical Society, Vol. 34, page 393, shows conclusively that this salt is the best reagent known for the accurate determination of the value of permanganate solutions.

is equivalent to 0.83344 gramme iron. Multiply this by .25 and .3, respectively, and divide by the number of c.c. of permanganate used. The result is the value of 1 c.c. of the permanganate in iron.

In all cases the mode of procedure in using the reductor should be as follows. Everything being clean and in good order from previous treatment with dilute sulphuric acid, and washing with distilled water, and the flask being attached to the filter pump, pour 100 c.c. of warm dilute sulphuric acid into the funnel and open the stopcock *c*. When only a little remains in the funnel forming the top of the reduction tube, transfer the solution to be reduced to the funnel. This solution should be hot but not boiling. Pour some of the dilute sulphuric acid into the vessel which contained the solution to be reduced to wash it, and when only a little solution is left in the funnel as before, add this to the funnel in such a way as to wash it and follow with about 200 c.c. more of warm dilute sulphuric acid and finally with 50 c.c. of hot distilled water. In no case allow the funnel to get empty, and close the stopcock *c* when there is still a little of the wash-water left in the funnel above the surface of the zinc. This precaution prevents air from passing into the reductor tube. A blank determination is made by passing through the reductor a solution containing a mixture of 10 c.c. strong sulphuric acid, 10 c.c. dilute ammonia, and 50 c.c. water; preceded and followed by the dilute acid as described above. The amount of potassium permanganate required to give this blank a distinct color is subtracted from the amount required to give the same color to each reduced solution.

To get the value of the permanganate solution multiply the value of 1 c.c. in iron by 0.88163 the ratio of molybdic acid to iron and the product by 0.01794 the ratio of phosphorus to molybdic acid and the result is the value of 1 c.c. of the permanganate solution in terms of phosphorus. The ratio of molybdic acid to iron given above is that found when a known amount of molybdic acid in sulphuric acid solution is passed through the reductor in the manner described above and then titrated with potassium permanganate solution whose strength in terms of metallic iron is known. The reduction of the molybdic acid in the reductor in this case is to the form $Mo_{24}O_{37}$. The ratio of phosphorus to molybdic acid given above is that found by the analysis of the yellow precipitate of ammonium

phospho-molybdate obtained from nitric acid solution of iron under varying conditions.

Sulphurous Acid.—A strong solution of the gas in water. Siphons of the liquefied gas may be obtained in the market.

Acid Ammonium Sulphite.—The strong C. P. solution of the reagent diluted with 10 parts of water.

Ferrous Sulphate.—Crystals of the salt free from phosphorus.

Sodium Thiosulphate.—Crystals of the salt free from phosphorus.

These four reagents are for reducing the excess of binoxide of manganese thrown down in oxidizing the carbonaceous matter in the nitric acid solutions of the steels. Any one may be used.

Molybdate Solution.—Place in a beaker 100 grammes of pure molybdic anhydride, mix it thoroughly with 400 c.c. cold distilled water and add 80 c.c. strong ammonia (0.90 sp. gr.). When solution is complete, filter and pour the filtered solution slowly and with constant stirring into a mixture of 400 c.c. strong nitric acid (1.42 sp. gr.) and 600 c.c. distilled water. Add 50 milligrammes of microcosmic salt dissolved in a little water, agitate thoroughly, allow the precipitate to settle for twenty-four hours, and filter before using.

Acid Ammonium Sulphate Solution, for washing the precipitate of ammonium phospho-molybdate. To 1 litre of water add 15 c.c. of strong ammonia (0.90 sp. gr.) and 25 c.c. strong sulphuric acid (1.84 sp. gr.).

Amalgamated Zinc.—Dissolve 5 grammes of mercury in 25 c.c. strong nitric acid diluted with an equal bulk of water, dilute to 250 c.c. and transfer to a stout flask of about 1000 c.c. capacity. Pour into it 500 grammes of granulated zinc which will pass through a 20-mesh sieve, but not through a 30-mesh. Shake it thoroughly for a minute or two and then pour off the solution, wash the zinc thoroughly with distilled water, dry, and preserve in a glass bottle for use.

Operation

Weigh 2 grammes, or, in case of steels containing over 0.15 per cent. phosphorus, 1 gramme of the drillings and transfer them to a 250 c.c. Erlenmeyer flask, pour into the flask 100 c.c. of nitric acid (1.135 sp. gr.)

and cover with a small watch-glass. Heat until the solution is complete and nitric oxide is boiled off. Add 10 c.c. of the strong potassium permanganate solution, boil until the pink color has disappeared and manganese dioxide separates. Continue the boiling for several minutes, then remove from the source of heat and add a few drops of sulphurous acid, a small crystal of ferrous sulphate, or a solution of 0.5 gramme of sodium hyposulphite in 10 c.c. of water, repeating the addition at short intervals until the precipitated manganese dioxide is dissolved. Boil two minutes longer, place the flask in a vessel of cold water, or allow it to stand in the air until it feels cool to the hand, and then pour in 40 c.c. of dilute ammonia (0.96 sp. gr.). The precipitated ferric hydrate will redissolve when the liquid is thoroughly mixed. When the solution is about the temperature of the hand, say 35° C.,* add 40 c.c. of molybdate solution at the ordinary temperature, close the flask with a rubber stopper, and shake it for five minutes, either by hand or in the machine, Fig. 48. Allow the precipitate to settle for a few minutes, filter on a 0.090 m. filter, and wash with acid ammonium sulphate solution until 2 or 3 c.c. of the wash-water give no reaction for molybdenum with a drop of ammonium sulphide. Pour 5 c.c. of ammonia (0.90 sp. gr.) and 20 c.c. of water into the flask to dissolve any adhering ammonium phospho-molybdate and then pour it on the precipitate in the filter, allowing the filtrate to run into a 250 c.c. beaker. Wash out the flask and wash the filter with water until the solution measures about 60 c.c. Add to the liquid in the beaker 10 c.c. strong sulphuric acid and pass it through the reductor exactly in the manner described for the solution of ferric sulphate in standardizing the solution of potassium permanganate, being careful to keep the end of the small tube of the reductor just below the surface of the liquid in the flask. By adding the strong sulphuric acid to the ammoniacal solution immediately before passing it through the reductor it is heated sufficiently by the chemical action to insure thorough

* When the steel contains vanadium or when its presence is suspected, add 5 c.c. of a saturated solution of ferrous ammonium sulphate and 2 or 3 drops sulphurous acid, which reduces the vanadium to the vanadyl condition, which does not interfere with the precipitation of the ammonium phospho-molybdate. This was suggested by Brearly and Ibbotson, Steel and Iron Anal. The reducing agents should be added to the cold solution and the shaking continued for at least 10 minutes until the gas formed has been liberated.

reduction. In washing be careful that no air passes into the reductor, and when the water has been drawn through, leaving a little still remaining in the funnel, close the stopcock, detach the flask F, wash off the drawn-out portion of the reductor tube into it, and titrate the solution with the standard permanganate. The reductor should be so arranged that the whole reduction occupies about three or four minutes. The solution that passes through should be bright green in color. In adding the permanganate, the green color disappears first, and the solution becomes brown, then pinkish yellow, and ultimately colorless. Continue the addition of the permanganate drop by drop, shaking the flask vigorously until the solution assumes a faint pink coloration, which remains after standing one minute. Subtract from the reading of the burette the amount given by a blank determination, obtained exactly as described under the method given above for standardizing the permanganate solution, multiply the number of c.c. so obtained by the value of 1 c.c. in terms of phosphorus, multiply by 100 and divide by the weight taken, and the result is the percentage of phosphorus in the steel.

When a large number of analyses are to be carried along at once the following modification is recommended. Obtain the yellow precipitate and dissolve in ammonia exactly as described above, except that the solution is allowed to run into the flask in which the precipitation was made, and the washing of the filter is continued until the solution amounts to 75 c.c. Add now to the flask 5 grammes of pulverized zinc, 100-mesh, pouring it into the flask through a funnel to prevent any zinc clinging to the sides of the flask. Then add to the flask 15 c.c. strong sulphuric acid (1.84 sp. gr.). This is most conveniently done in practice by letting it run in from a glass-stoppered burette. Close the flask at once with a rubber stopper carrying a glass tube bent twice at right angles, the farther arm dipping into a beaker containing a saturated solution of sodium bicarbonate. The flask should now stand undisturbed for about thirty minutes, when, if all action has ceased, it is ready to titrate with permanganate. The solution should be green, not brown. The temperature of the solution at the end of thirty minutes is about 40° C. and the titration succeeds

best if done at this temperature. But the flask may stand a couple of hours without reoxidation of the reduced molybdic acid, and may then be successfully titrated. If the solution changes in color to brown the determination should be rejected, as the result will be too low. A blank should be made by adding to another flask 65 c.c. of water, 10 c.c. of dilute ammonia (0.96 sp. gr.), 5 grammes of the 100-mesh zinc, added in the manner described, and 15 c.c. of strong sulphuric acid (1.84 sp. gr.). This flask should be treated the same as the others and the amount of permanganate it uses up should be deducted from the amount required by each flask containing a test. When this method is used the reduction is practically complete to molybdic acid, so that the factor 0.85714 must be used instead of 0.88163.

Example

Then multiplying the value in iron by the ratio of molybdic acid to iron 0.88163 or 0.85714 and the product by the ratio of phosphorus to molybdic acid 0.01794, we have $0.0034923 \times 0.88163 \times 0.01794$ equals 0.000055238, or 1 c.c. permanganate equals 0.000055238 gramme of phosphorus. Again, the precipitated ammonium phospho-molybdate from 2 grammes of steel required 35.6 c.c. permanganate less blank 0.1 c.c. equals 35.5 c.c.; $35.5 \times 0.000055238 \times 100 \div 2$ equals 0.098 per cent. phosphorus.

Notes and Precautions

It will be observed that the method given above oxidizes the phosphorus in the iron by means of nitric acid, completes and perfects this oxidation and possibly neutralizes the effect of the carbon present by means of potassium permanganate, and then separates the phosphoric acid from the iron by means of molybdic acid. The molybdic acid in the yellow phosphomolybdate is subsequently determined by means of potassium permanganate, the phosphorus being determined from its relation to the molybdic acid in this precipitate. The method given above applies to steel and wrought iron, but it is not yet recommended for pig-iron.

It is hardly necessary to say that all the chemicals and materials used in the analysis are assumed to be free from impurities that will iniuriously affect the result.

1.135 sp. gr. nitric acid apparently oxidizes the phosphorus just as successfully as a stronger one, while by its use solution is sufficiently rapid, and there is less trouble during the subsequent filtration due to silica.

The boiling of the solution to remove nitrous acid and assist the action of the oxidizing permanganate seems to be essential. Some steels may not require 10 c.c. of the permanganate and some, like washed metal high in carbon, may require even more. It is essential that enough should be added to cause a precipitation of manganese dioxide and to give a strong pink color to the solution. This color gradually disappears on boiling. Less is required if the permanganate is added in small successive portions. Boiling two minutes after reducing the manganese dioxide removes any nitrous acid that may be formed by that operation.

In washing the yellow precipitate it shows some disposition to crawl up to the top of the filter. Care should therefore be taken to have the filter fit the funnel so closely that even if the precipitate does crawl over the top it will not be lost while washing the filter completely to the top. It is very easy to leave enough molybdic acid in the top of the filter, even though the washings are tested, to cause an error of .005 per cent. in the determination.

In certain cases the solution that passed through the reductor was *brown* instead of green, especially when working on steels containing 0.1 per cent. phosphorus or over. This was not the case when an equivalent amount of molybdic acid was dissolved in ammonia and treated in the same way. Experiments seemed to prove that the chemical change from the phospho-molybdate to ammonium phosphate and ammonium molybdate did not occur immediately, but that a certain interval was necessary for the completion of the reaction. One-tenth gramme portions of ammonium phospho-molybdate were taken and dissolved in 10 c.c. of ammonia. Those acidulated with sulphuric acid and 2 c.c. in excess added and passed through the reductor at once were all brown in color and gave varying results on titration wth permanganate. Others after standing several days and then acidulated and passed through the reductor gave bright green solutions and perfectly agreeing and satisfactory results. The same results were obtained by heating the ammoni-

acal solutions for 15 to 20 minutes nearly to boiling, cooling, acidulating and passing through the reductor.

It is best to make up molybdic solution rather frequently. It is also best to keep it in the dark at a temperature not above 28° or 30° C. Much of the so-called molybdic acid of the market is ammonium molybdate or molybdate of some other alkali. This fact cannot be ignored in making up the molybdate solution. A series of experiments with various molybdic acids and alkaline molybdates obtained in the market indicates that if the amount of molybdic acid in the solution is that called for by the formula, irrespective of whether this amount is furnished by pure molybdic acid or by any of the commercial molybdates referred to, the result will be much nearer the truth than if this is not done. Good molybdic acid is the best, but the alkaline molybdates can be used. The amount of molybdic acid in these molybdates can readily be determined by dissolving 0.1000 gramme in 60 c.c. of water to which 10 c.c. of dilute ammonia have been added, filtering, adding 10 c.c. strong C. P. sulphuric acid, and passing through the reductor as above described. The method given in the example above enables the amount of molybdic acid to be determined. If the molybdic acid as obtained in the market, or the ammonia used in dissolving it, contains any soluble silicates, the resulting molybdate solution will be yellowish in color and the determination made with this solution will be high, owing apparently to ammonium silico-molybdate being dragged down with the phospho-molybdate. Treatment of the molybdate solution with microcosmic salt, as described, overcomes this difficulty and gives a perfectly colorless molybdate solution. A molybdate solution tinged with yellow should never be used. It will be observed that the molybdate solution recommended above contains much less ammonium nitrate than is given by many of the formulas now in use. Experience shows that a molybdate solution made on this formula keeps much better than those containing more ammonium nitrate. It will also be observed that the amount used for each determination is less than many methods employed. It is believed that the amount recommended is sufficient and that the ammonium nitrate required to assist the formation of the yellow precipitate is furnished by the 40 c.c. of dilute ammonia added to the nitric acid solution of the steel. Of course the molybdate solution recom-

mended above cannot be used for other work interchangeably with that made on the older formulas, on account of lack of ammonium nitrate.

The directions in regard to the reductor, both as to making and use, should be strictly followed. By the use of the stopcock and the amalgamated zinc, and by keeping a little liquid in the funnel, the same blank can be obtained from a reductor almost continuously, even though two or three days of standing intervene between blanks. It is, however, always advisable to treat with dilute sulphuric acid and wash before using, even though only one night has elapsed since the last previous use. If the solution to be reduced does not contain enough acid or is not warm enough, the reduction will not be complete. Care should therefore be taken not to allow too much mixing of the dilute sulphuric acid with the solution to be reduced, either in the funnel or in the reductor tube itself. The best asbestos to use is the mineral known as actinolite, but any fibrous mineral which will act as a filter and not be dissolved by the acids used may be employed. Glass wool alone will not do, as a good filter is essential in order that neither small particles of zinc nor impurities in the zinc may be drawn down into the flask with the reduced solution. The consumption of zinc is very small.

In testing with ammonium sulphide, to see whether the washing of the yellow precipitate is complete, good results are obtained by putting two or three drops of yellow ammonium sulphide into a few cubic centimetres of distilled water, and allowing the washings to drop into this solution from the stem of the funnel. If iron is present in the washings it will show while the solution is still alkaline. By allowing the washings to continue running into the ammonium sulphide solution it soon becomes acid, when molybdenum, if any is present, shows by a more or less brownish color. If the acid solution is pure white from separated sulphur the washing is complete.

Since the acidity of the solution in which the yellow precipitate is formed has an influence on its composition, it is quite desirable that the sp. gr. of the 1.135 nitric acid and of the 0.96 ammonia should be taken with some care. The temperature at which the figures are correct is 15° C. It is best to use the Westphal balance in determining these gravities, but, failing this, a sufficiently delicate hydrometer may be employed.

In using the reduction with 5 grammes of 100-mesh zinc, it will be observed that as the zinc becomes nearly all dissolved a blackish residue remains. This residue seems to be metallic lead. It disappears slowly during the titration and apparently uses up some permanganate. It takes a little longer to secure a satisfactory end reaction with the 100-mesh zinc, as the pink color fades out several times before it will remain permanent for one minute. It is essential that air should be excluded from the flask after the reduction is nearly complete, and it is for this purpose that the sodium bicarbonate solution is used. A tendency to suck the soda solution back into the reducing flask will be noticed, due to the cooling of the flask. The reduction should be made in a place free from draughts.

With the amalgamated zinc in the reductor made as above described the blank generally uses up about 0.1 c.c. of the standard permanganate solution. The blank when using the reduction by means of 5 grammes 100-mesh zinc usually amounts to 0.6 c.c. of the standard permanganate, and may be higher. Pulverized zinc is rarely free from sulphides, and while this seems not to be a very important matter, it is nevertheless not recommended to use, either in the reductor or in the flask reduction, a zinc that gives a high blank.

If the amount of sulphurous acid or other reagent added to the nitric acid solution to remove the precipitated binoxide of manganese is insufficient, a brown stain will be left on the filter-paper after the yellow precipitate is dissolved in ammonia. This may occur even though the nitric acid solution looks clear, and as no harm can arise from a slight excess of the reducing agent, it is usually more satisfactory to add an excess. It is not desirable to add the reducing agent to the solution while boiling, as under such circumstances it frequently boils over.

It is rather essential to use the dilute sulphuric acid warm, so that the general temperature of the reductor may be kept up.

Determination of Phosphorus in Pig Iron

When pig iron is dissolved in nitric acid the silica formed from the silicon becomes gelatinous and makes the solution very difficult to filter, and if hydrofluoric acid is added the hydrofluoric acid interferes with the precipitation of the phospho-molybdate. It is therefore best to pro-

ceed as follows: Treat 2 grammes of the sample (1 gramme in high phosphorus pig) with 25 c.c. of nitric acid and 25 c.c. water. When decomposition is complete add a little hydrochloric acid and evaporate to dryness. Dissolve in hydrochloric acid and evaporate again. Redissolve in 15 c.c. hydrochloric acid, dilute with 30 c.c. water, filter and wash. Evaporate the filtrate almost to dryness. Ignite the insoluble matter, burn off the graphite, and treat with two or three drops of sulphuric acid and a little hydrofluoric acid. Evaporate to dryness, ignite, and dissolve the residue in hydrochloric acid. Add this solution to the filtrate, evaporate twice with nitric acid, transfer to a flask, and precipitate as on page 93.

Alkalimetric Method *

The principle on which this method is based is the acidity of ammonium phospho-molybdate, which, according to the following reaction, requires 23 molecules of alkali for its neutralization.

$$2[(NH_4)_3 12MoO_3PO_4] + 46NaHO + H_2O = 2[(NH_4)_2HPO_4] + (NH_4)_2MoO_4 + 23Na_2MoO_4 + 23H_2O$$

Reagents

Molybdate Solution.—The solution described in the last method (page 92) may be used.

Nitric Acid for Washing Precipitates.—A 1 per cent. solution of nitric acid: add 13 c.c. of strong nitric acid (1.42 sp. gr.) to 1 litre of water.

Potassium Nitrate Solution.—A 1 per cent. solution of potassium nitrate: dissolve 10 grammes of potassium nitrate in 1 litre of water.

Phenolphthalein Solution.—A 0.2 per cent. solution of phenolphthalein: dissolve 1 gramme of phenolphthalein in 500 c.c. of 95 per cent. alcohol.

Standard Solution of Sodium Hydroxide. — To 100 grammes pure sodium hydroxide add an amount of water just insufficient to completely dissolve it. Pour it into a tall cylinder, close the cylinder and allow the insoluble matter, sodium carbonate, etc., to settle. The clear liquid

* This method was first suggested by Mr. C. E. Manby and subsequently modified by Mr. James O. Handy, of Pittsburg, to whose work many of the details are due. It is quite extensively used and is extremely rapid. Mr. Handy kindly prepared the essential part of this description.

will be practically free from carbonate. Dilute it in the proportion of 30 c.c. to 2 litres of water.

Standard Nitric Acid.—Measure 2 litres of water into a glass-stoppered bottle, add 20 c.c. of nitric acid (1.42 sp. gr.) and mix thoroughly. Measure accurately 10 c.c. of the "Standard Solution of Sodium Hydroxide." Place them in a small flask, add 40 c.c. of water and 3 drops of "Phenolphthalein Solution." Drop "Standard Nitric Acid" from a carefully calibrated burette into the flask until the pink color just disappears. If the solutions are not of the same strength, dilute the stronger with water until they agree. For example, if it required 9.5 c.c. of nitric acid to discharge the color, return the nitric acid from the burette to the bottle and dilute it according to the following proportion: 9.5 : 10 = 2030 (the volume of nitric acid remaining) : 2136.9.

Add 106.9 c.c. of water to the nitric acid, and after thoroughly mixing it retest as above.

If it should require 10.5 c.c. of the nitric acid solution to discharge the color, dilute the sodium hydroxide solution according to the proportion: 10 : 10.5 = 2010 (the volume of sodium hydroxide remaining) : 2110.5.

Add 100.5 c.c. of water to the solution of sodium hydroxide, mix thoroughly, and retest.

The standard solutions being equal in strength, standardize them as follows:

Titrate the ammonium phospho-molybdate obtained from a steel in which the phosphorus has been carefully determined, and divide the percentage of phosphorus by the number of c.c. of the "Standard Solution of Sodium Hydroxide" required to neutralize it. The result is the value of the "Standard Solution of Sodium Hydroxide."*

Operation

Precipitate the ammonium phospho-molybdate from 2 grammes of the steel exactly as described in the last method "Reduction by Zinc and Titration by Permanganate Solution."

* Mr. Handy prefers to have the solutions of such strength that 1 c.c. = 0.0002 gramme phosphorus. To obtain this result calculate the weight of phosphorus to which each c.c. of the solutions is equivalent and dilute them as required.

Filter and wash first with "Nitric Acid for Washing Precipitates" and then with "Potassium Nitrate Solution" until the washings are no longer acid. Place the filter and precipitate in the flask in which the precipitation was made and run in from a pipette 10 c.c. of the "Standard Solution of Sodium Hydroxide." If, after agitation, this is insufficient to dissolve the precipitate, add 10 c.c. more, and if necessary continue the additions until the precipitate is dissolved. Dilute to 50 c.c., add 3 drops "Phenolphthalein Solution," and add from a burette "Standard Nitric Acid" until the pink color disappears. Subtract the number of c.c. of "Standard Nitric Acid" used from the number of c.c. of "Standard Solution of Sodium Hydroxide" taken to dissolve the precipitate, and the remainder will be the number of c.c. of the "Standard Solution of Sodium Hydroxide" required to neutralize the ammonium phospho-molybdate. From this calculate the amount of phosphorus in the steel.

Direct Weighing of the Phospho-Molybdate
High Phosphorus Irons

For foundry and other high phosphorus pig-irons dissolve 1 gramme of the drillings in a 250 c.c. beaker in 25 c.c. of nitric acid 1.135 sp. gr. with the addition of a little hydrochloric acid. Evaporate to dryness, redissolve in hydrochloric acid, evaporate to dryness and heat for half an hour in the air-bath at a temperature of at least 200° C. Redissolve in 10 c.c. hydrochloric acid, dilute, filter and wash. Receive the filtrate in a 400 c.c. beaker and evaporate to syrupy consistency. Ignite the filter containing the insoluble matter and if it is desired to determine the silicon, burn off the graphite and weigh. Treat the material in the crucible with hydrofluoric acid with a few drops of sulphuric acid, evaporate to dryness, ignite and weigh. The loss of weight is Silica, which multiplied by .4693 gives the Silicon. Dissolve the residue in the crucible in hydrochloric acid and add it to the solution in the beaker. Add 25 c.c. nitric acid to the syrupy solution in the beaker and boil down to a few c.c., add 25 c.c. more of nitric acid and boil again to decompose all the hydrochloric acid. Transfer the solution to a 250 c.c. Erlenmeyer flask, using about 20 c.c. of water and 75 c.c. of nitric acid 1.135 sp. gr. for washing out the beaker. Precipitate exactly as

directed on pages 92 and 93. Allow the precipitate to settle, filter on a Gooch crucible, wash several times with the solution of acid ammonium sulphate described on page 92, then with very dilute nitric acid and finally with cold water, dry at temperature of 110° C. for half an hour and weigh. The weight of the precipitate multiplied by 0.0163 gives the phosphorus. This factor is not the theoretical one based on the generally accepted composition of the ammonium phospho-molybdate, but is the one that seems to give the closest approximation to the true amount of phosphorus contained in the salt as it is obtained under the ordinary working conditions. The perforated porcelain crucibles now made are well adapted for use in this method.

Direct weighing of the phospho-molybdate is practically necessary in iron and steel containing more than .25 per cent. of phosphorus, as the amount that can be properly titrated is limited. Decreasing the amount of the sample taken for analysis multiplies the error and renders it difficult to get a proper average of the material.

The use of the Gooch crucible is almost universal, for in the absence of the ordinary filter pump the arrangement shown on page 22 can be used, so that the use of counterpoised filters is rarely necessary.

DETERMINATION OF MANGANESE

The Acetate Method

Dissolve 1 gramme of drillings in 15 c.c. nitric acid (1.2 sp. gr.) in a 250 c.c. beaker. Evaporate to dryness in the air-bath, and heat to decompose carbonaceous matter. Allow the beaker to cool, add 10 c.c. hydrochloric acid, heat carefully until all the ferric oxide is dissolved, evaporate to dryness to get rid of all the nitric acid, redissolve in 10 c.c. hydrochloric acid, and evaporate carefully until the solution is almost syrupy. Dilute with cold water to about 100 c.c., and filter off the insoluble matter, allowing the filtrate and washings to run into a No. 6 Griffin's beaker. In the case of steel or puddled iron the filtration may be omitted, the solution being poured into the large beaker, and the rinsings of the small beaker added. To the solution in the large beaker, which should amount to about 200 c.c., add a solution of sodium carbonate very slowly, stirring vigorously. The solution will finally be-

come very dark red in color, and the precipitate formed will redissolve very slowly. Add the solution of sodium carbonate 2 or 3 drops at a time, stir well, and allow the solution to stand several minutes, to see whether or not the precipitate will redissolve. When, under these circumstances, a decided precipitate remains, add 2 drops of hydrochloric acid, stir well, and allow the solution to stand for some minutes; if the solution does not clear, add 2 drops more, and stir again. If the first part of the operation has been carefully conducted, this amount of hydrochloric acid will usually be sufficient, but if, for any reason, too large a precipitate has been formed, it may require a few drops more. It is important, however, that no more hydrochloric acid be added than just enough to redissolve the precipitate formed by the sodium carbonate, and, to insure this, the solution should be well stirred and allowed to stand a sufficient length of time after each addition of hydrochloric acid. The solution may be so dark in color that it is difficult to see when the precipitate does finally disappear, but by standing the beaker on a piece of white paper the light reflected through the bottom of the beaker will greatly diminish the difficulty. When, under this method of procedure, the solution clears, add 2 grammes of sodium acetate dissolved in a few c.c. of water, stir well, and dilute the solution to about 700 c.c. with boiling water. Heat it to boiling, and allow it to boil for about ten minutes, then remove it from the tripod, and allow the precipitated ferric hydrate and acetate to settle. Decant the clear, supernatant fluid on a large washed filter, throw the precipitate on, and wash it two or three times with boiling water, allowing the filtrate to run in a large beaker or flask, from which it can be transferred to a platinum or porcelain dish and evaporated rapidly. When the precipitate has drained quite dry, by means of a platinum spatula transfer it to the beaker in which the precipitation was first made; dissolve the precipitate which remains adhering to the filter, and that which remains on the blade of the spatula, by pouring around the edge of the filter and on the spatula held over it 10 c.c. hydrochloric acid diluted with twice its volume of hot water, and heat the beaker containing the precipitate. Wash the filter free from ferric chloride with cold water, and heat the beaker containing

the precipitate until the latter is dissolved. Cool the solution, and repeat the precipitation, filtration, and re-solution of the precipitate precisely as in the first case, adding this filtrate to the first one. Precipitate, filter, and wash a third time in the same manner, evaporate all the filtrates together until they are reduced to about 300 c.c. in volume, and transfer this solution to a 600 c.c. beaker.

If during the evaporation any manganese has become oxidized by exposure to the air, it forms a hard ring on the side of the capsule, and may be dissolved, after the solution is poured into the beaker, by two or three drops of hydrochloric acid, and washed into the beaker. Should any ferric oxide separate out, pour the solution in the capsule through a small filter, allowing it to run into the beaker, wash the precipitate with hot water, dissolve it in a very few drops of dilute hydrochloric acid, and let it run into a 150 c.c. beaker. Add just enough solution of sodium carbonate to precipitate it, make it faintly acid with acetic acid, boil it, and filter into the main solution.

This solution now contains all the manganese, nickel, and cobalt and the greater part of the copper which may have been in the metal. Add to it 10 grammes of sodium acetate and a few drops of acetic acid, heat it to boiling, and pass a current of hydrogen sulphide through the boiling solution for fifteen minutes. This will precipitate the copper, cobalt, and nickel. Filter off the black sulphides, boil the filtrate to expel the excess of hydrogen sulphide, let the solution cool somewhat, and add bromine-water in excess. If no precipitate forms at first, stand the solution, which should be colored by the bromine-water, in a warm place for an hour or two, to allow the precipitate of manganese dioxide to separate out. If a precipitate forms immediately, add bromine-water until, when the precipitate settles, the solution is strongly colored by it, and stand it aside for an hour or two. At the end of this time, the precipitate having settled and the supernatant fluid being still colored by the bromine, heat it carefully, finally to boiling, and expel the excess of bromine; allow the precipitate to settle, filter, wash very carefully, and avoid stirring up the precipitate when it is on the filter, as it has a tendency to go through. Dissolve the precipitate on the filter in sulphurous acid water containing a little hydrochloric acid; allow the solution to run into a platinum dish, and wash the

filter well. A little of the sulphurous acid water will quickly dissolve any manganese dioxide which may adhere to the beaker in which it was precipitated, and this may be poured on the filter. Boil the solution in the dish to expel the excess of sulphurous acid, add from 5 to 20 c.c. of a clear filtered solution of microcosmic salt, heat to boiling, and add ammonia, drop by drop, with constant stirring. When the precipitate of ammonium-manganese phosphate begins to form, stop adding ammonia, and stir until the precipitate becomes crystalline. When this change occurs, add one more drop of ammonia; the additional precipitate formed will be curdy, but a few seconds' continued stirring at the boiling temperature will change it to the silky crystalline condition. Continue the addition of ammonia in exactly the same manner until the precipitate is all down and further additions of ammonia fail to change the silky appearance. Add a dozen drops of ammonia in excess, remove the dish from the light, and stand it in ice-water until perfectly cold. Filter on an ashless filter, wash with cold water containing 10 grammes of ammonium nitrate (dissolved in water made faintly alkaline with ammonia and filtered) in 100 c.c. until the filtrate gives no reaction for hydrochloric acid, dry, ignite, and weigh as manganese pyrophosphate, which contains 38.69 per cent. manganese. During the precipitation of the ammonium-manganese phosphate the stirring must not be discontinued for an instant, as the solution has a great tendency to bump when the precipitate is allowed to settle. The crystalline condition of the precipitate, which is absolutely necessary for the success of the determination, can most readily be brought about by the means described above. It can, of course, be accomplished by adding an excess of ammonia at once, but it will require much more boiling and stirring than the method above described. The final precipitation as ammonium-manganese phosphate, due to Dr. Gibbs, is much the most accurate method known. A common practice, however, is to wash the bromine precipitate of hydrated manganese dioxide, dry, ignite, and weigh as manganoso-manganic oxide, which contains 72.03 per cent. manganese. There are two objections to this method of procedure: first, the difficulty of washing the manganese dioxide free from sodium salts; secondly, the uncertainty as to the exact state of oxidation of the ignited manganese oxide.

The first of these objections Eggertz claims to overcome by washing the precipitated manganese with water containing 1 per cent. of hydrochloric acid. It may also be overcome, or rather the danger may be avoided, by using no fixed alkalies. By this method, nearly neutralize the hydrochloric acid solution of the iron or steel by ammonia, then add a solution of ammonium carbonate exactly as directed above for sodium carbonate, and finally, instead of sodium acetate, add ammonium acetate (5 c.c. of ammonia slightly acidulated by acetic acid). Evaporate the filtrates obtained in this way to about 500 c.c., transfer to a flask of about 1 litre capacity, and cool. When perfectly *cold*, add 3 or 4 c.c. bromine, shake well, and when the solution is strongly colored all through by bromine, add an excess of ammonia, and heat to boiling. Filter, wash with hot water, dry, ignite, and weigh as manganoso-manganic oxide.

The second objection seems, according to Pickering,* to be well founded, the amount of manganese in the ignited oxides varying from 69.688 per cent. to 74.997 per cent., according to the temperature to which they were heated and other undetermined conditions. This cause of error may be avoided by weighing the precipitate as manganous sulphide, containing 63.15 per cent. manganese. This method, due to H. Rose,† is carried out as follows: Ignite the oxide in a porcelain crucible, allow it to cool, mix it with five or six times its volume of flowers of sulphur, place the crucible on a triangle, and insert the bowl of a clay tobacco-pipe, which should be large enough to quite fill the top of the crucible and too large to reach the precipitate. Pass through the stem a current of dry hydrogen until all air is expelled, heat the crucible gradually to as high a heat as a good Bunsen burner will produce, cool in the current of hydrogen, and weigh as manganous sulphide.

General Remarks on the Acetate Method

The chief source of error in the acetate method, as it is usually practiced, is in the addition of too much sodium acetate, whereby the manganous chloride is changed to manganous acetate, which, according to Kessler,‡ is readily decomposed to manganous oxide and acetic acid.

* Chem. News, xliii. 226.

† Rose, Quant. Anal. (French ed.), p. 104.

‡ Chem. News, xxvii. 14.

Under these circumstances, a larger amount of manganese is precipitated with the iron than would be the case if a less amount of sodium acetate were added. When sodium acetate is added to ferric chloride, the reaction may be written, $6NaC_2H_3O_2,3H_2O + Fe_2Cl_6 = 6NaCl + Fe_2(C_2H_3O_2)_6 + 3H_2O$; and to precipitate the iron as ferric acetate in 1 gramme of metal would necessitate the use of 8 grammes of sodium acetate. But, as Kessler in the same article remarks, when a solution of ferric chloride is treated with sodium carbonate and hydrochloric acid exactly as described above, a liquid is formed which contains fourteen times its equivalent of *ferric hydrate* in solution. Consequently ½ gramme of sodium acetate would be sufficient to precipitate 1 gramme of iron as ferric hydrate and basic acetate. In order, however, to precipitate the manganese as manganese dioxide by bromine, it is necessary to convert all the manganous chloride into manganous acetate: consequently an excess of sodium acetate is added before adding bromine. If, when making the acetate precipitation, the solution contains any ferrous chloride, a "brick-dust" precipitate is usually formed, which generally passes through the filter, and is very difficult to dissolve or manage in any way. It is usually the shortest and best plan, in this event, to start a fresh portion and throw away the other.

The Nitric Acid and Potassium Chlorate Method

(*Ford's Method*)

The acetate method is at best very tedious, and when the amount of manganese is very small it is of course desirable to work on larger amounts than 1 gramme of the sample, but in this event the iron precipitate is so large that it becomes very difficult to manage it properly. With Ford's method, however, there is almost no limit to the amount which can be operated upon, and many experiments have shown that with proper precautions it is an extremely accurate process. The reaction on which the process is based was first noticed by Hannay * in 1878; but Ford † first worked out the method in its present practical form. Dissolve 5 grammes of borings in a 400 c.c. beaker in 60 c.c. nitric acid (1.2 sp. gr.), evaporate down until the solution is almost syrupy, then add 100 c.c.

* Jour. Chem. Soc., xxxiii. 269. † Trans. Inst. Min. Engineers, ix. 397.

strong nitric acid (1.4 sp. gr.) and 5 grammes potassium chlorate. Heat the solution to boiling either on the hot plate or on a tripod with a thin piece of sheet asbestos, about 1 inch (25 mm.) in diameter, on the centre of the wire gauze. Boil the solution fifteen minutes, remove the light, add 50 c.c. strong nitric acid and 5 grammes potassium chlorate, replace the light, and boil fifteen minutes longer, or until the yellowish fumes from the decomposition of the potassium chlorate are no longer given off. Cool the solution as rapidly as possible by standing the beaker in cold water, filter on the pump, using the cone* or glass filtering-tube with asbestos filter,† and wash two or three times with strong nitric acid, which must be free from nitrous fumes.‡ Nitrous acid reduces manganese dioxide to manganous oxide, which then dissolves in nitric acid. Its presence may be recognized by the yellow color it imparts to nitric acid, and it may be removed by blowing air through the acid. It is always formed in nitric acid which has been exposed to sunlight, and for that reason this acid should be kept in a dark place. Suck the precipitate dry, and transfer it, with the asbestos filter, to the beaker in which the precipitation was made. Pour into the beaker from 10 to 40 c.c. strong sulphurous acid water, which will dissolve the precipitate almost instantly. By pouring it through the cone or filtering-tube, any adhering precipitate will be dissolved and carried into the beaker. As soon as the precipitate is dissolved, filter from the asbestos into a 150 c.c. beaker, washing with hot water, and add to the filtrate from 2 to 5 c.c. hydrochloric acid. Heat the filtrate until the excess of sulphurous acid is driven off, add bromine-water until the solution is strongly colored with it, and boil off the excess of bromine. Add ammonia until the solution smells quite strongly of it, boil for a few minutes, and filter into a 400 c.c. beaker. Wash several times with hot water, remove the beaker, dissolve the ferric hydrate on the filter in dilute hot hydrochloric acid (1 part of acid to 3 of water), allowing the solution to run back into the beaker in which the precipitation was made, and wash the filter with hot water. Boil this filtrate for a few minutes to

* See page 24.

† As described under Methods for Determination of Carbon.

‡ It is always well to transfer the filtrate and washings to a 600 c.c. beaker, add 2 grammes potassium chlorate, and boil again, to see whether any further precipitate of manganese dioxide is formed.

drive off the chlorine which may be present from the solution of any little manganese dioxide precipitated with the ferric hydrate, reprecipitate by ammonia as before, filter, and repeat the solution, precipitation, and filtration, allowing all the filtrates from the ferric hydrate to run into the 600 c.c. beaker. Acidulate this solution, which will be about 300 or 400 c.c. in volume, with acetic acid, heat to boiling, and pass hydrogen sulphide through the boiling solution for ten or fifteen minutes. Filter into a platinum dish from any cobalt sulphide, which is the only metal likely to be present with the manganese; boil off the hydrogen sulphide after adding a little hydrochloric acid, add microcosmic salt, and precipitate, filter, ignite, and weigh, as directed on pages 105 and 106, as manganese pyrophosphate.

Steels Containing Much Silicon

In steel high in silicon (0.2 per cent. and over) the gelatinous silica formed is very apt to clog the filter when operating as described above, and it is better to dissolve the sample in hydrochloric acid, evaporate to dryness, being careful not to heat it too hot, redissolve carefully in 50 c.c. strong nitric acid, boil down until nearly syrupy to destroy all the hydrochloric acid, redissolve in 100 c.c. strong nitric acid, and precipitate as directed above.

Instead of dissolving in hydrochloric acid, Mr. Wood suggests adding a few drops of hydrofluoric acid to the nitric acid solution before evaporating. This seems to work extremely well, and saves much time in the case of high silicon steels. It may also be used to advantage in the case of pig-iron instead of the method given below.

Pig-Iron

Dissolve 5 grammes in 50 c.c. dilute hydrochloric acid (1 part hydrochloric acid to 1 part water), filter on a washed filter into a 400 c.c. beaker, evaporate to dryness, redissolve in 50 c.c. strong nitric acid, and proceed as in the case of "steel high in silicon."

Spiegel and Ferro-manganese

It is best to use only 1 gramme of spiegel or ferro-manganese of from 20 to 40 per cent. manganese and .5 gramme or $\frac{1}{10}$-factor weight of very

high (from 60 to 80 per cent.) ferro-manganese. In the latter, indeed, it is better to use the acetate method with ammonia and acetic acid, and, omitting the precipitation by bromine, boil off the hydrogen sulphide from the filtrate from the insoluble sulphides, after adding hydrochloric acid, and then precipitate by microcosmic salt as directed above.

RAPID METHODS

Volumetric Methods

Volhard's Method *

This method is based on the principle announced by Morawski and Stingl,† that when potassium permanganate is added to a neutral manganous salt all the manganese is precipitated, in accordance with the reaction $4KMnO_4 + 6MnSO_4 + 4H_2O = 10MnO_2 + 4KHSO_4 + 2H_2SO_4$. When all the manganous salt is oxidized, the solution is colored by the permanganate, which thus indicates the end reaction. The permanganate used for titrating iron ores may be used for this determination, and, its value being determined, as directed, in terms of iron, the calculation for manganese is as follows. The reaction, when permanganate is added to a solution of ferrous sulphite, is $10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O$, or 2 molecules of potassium permanganate oxidize 10 molecules of ferrous sulphate. Now, as 2 molecules of permanganate oxidize 3 molecules of manganous sulphate, while 2 molecules of permanganate oxidize 10 molecules of ferrous sulphate, the oxidizing power of the permanganate is only three-tenths as great in the former case as it is in the latter, and its value in manganese is to its value in iron as 3 is to 10, or $\frac{55}{55}:\frac{93}{84} \times \frac{3}{10} = \frac{165}{55}:\frac{79}{84}$. Therefore the value of the permanganate in iron multiplied by $\frac{165}{55}:\frac{79}{84}$ or 0.2951 = its value in manganese.

Dissolve 1.5 grammes of borings in a platinum or porcelain dish in 25 c.c. nitric acid (1.2 sp. gr.). When solution is complete, add 12 c.c. dilute sulphuric acid (1 part concentrated sulphuric acid and 1 part water), and evaporate to dryness, as directed on page 20, heating until fumes of

* Liebig's Annalen, cxcviii. 318; Chem. News, xl. 207.
† Chem. News, xxxviii. 297.

sulphuric acid are given off in order to destroy all the carbonaceous matter. Or dissolve in nitric acid as above, evaporate to dryness, and heat on the tripod until the carbonaceous matter is destroyed; dissolve in 15 c.c. hydrochloric acid, add 12 c.c. dilute sulphuric acid as above, and evaporate until fumes of sulphuric acid are given off. Allow the dish to cool, add 100 c.c. water, and heat until the ferric sulphate is dissolved. Wash into a carefully graduated 300 c.c. flask, so that with the washings the solution may not exceed 200 c.c. in volume, and add a solution of sodium carbonate until the precipitate which is first formed dissolves only with difficulty. Then add slowly zinc oxide * suspended in water, shaking well after each addition until the iron is precipitated, which will be shown by the sudden coagulation of the solution. The precipitate will then settle, leaving a slightly milky supernatant liquid. Fill the flask exactly to the mark on the neck (300 c.c.), and mix thoroughly by pouring the entire contents of the flask into a large, clean, dry beaker, and back again into the flask, repeating this several times. Allow the precipitate to settle for a few minutes, and pour the solution through a large *dry* filter. Fill a 200 c.c. pipette with this filtrate, which will, of course, represent exactly 1 gramme of the sample, run it into a flask of about 500 c.c. capacity, heat to boiling, and add from 2 to 5 drops of nitric acid (sp. gr. 1.2). Now add permanganate solution slowly from a burette, shaking after each addition to mix the solution and facilitate the collection of the precipitated hydrated manganese dioxide. When the reaction is nearly finished, the solution will be slightly colored by the permanganate, but the color disappears after shaking the flask and allowing it to stand for a moment. Finally, however, a drop or two will give the solution a permanent pink color, which will not disappear for several minutes. The number of c.c. of the permanganate solution used multiplied by the factor found (the iron factor of the permanganate multiplied by 0.2951) is the amount of manganese in the sample. If, during the addition of the permanganate, the solution should become cool and the precipitate fail to collect and settle quickly, heat the solution, but not quite to the boiling-point. This method is appli-

* See page 54.

cable for all samples except those containing very minute amounts of manganese. In working on spiegel, take .75 gramme, then, using two-thirds of the filtrate, the amount will be calculated on .5 gramme.

Williams's Method

This method, which consists in precipitating the manganese dioxide by Ford's method, filtering, washing, dissolving in sulphuric acid with a measured volume of some reducing agent, such as oxalic acid or ferrous sulphate, and titrating the excess by permanganate, was first used by Williams.* Regarding the precipitate by potassium chlorate in a nitric solution as manganese dioxide, the reaction in dissolving it might be expressed thus: $MnO_2 + 2FeSO_4 + 2H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + 2H_2O$, or $MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2CO_2 + 2H_2O$. Therefore 1 molecule of manganese dioxide oxidizes 2 molecules of ferrous sulphate or 1 molecule of oxalic acid, and, the excess of oxalic acid or ferrous sulphate unoxidized having been determined by a solution of permanganate, the difference between this excess and the amount originally added is the amount oxidized by the manganese dioxide.

We therefore require two standard solutions, one of permanganate and one of ferrous sulphate, ammonium-ferrous sulphate, or sodium oxalate. The permanganate solution used for iron determinations answers perfectly. A solution of ferrous sulphate is perhaps the most satisfactory, and is prepared by dissolving 10 grammes of the crystallized salt, $FeSO_4$, $7H_2O$,† in 900 c.c. water and 100 c.c. strong sulphuric acid. It will keep prefectly in a glass-stoppered bottle in the dark for a long time. One c.c. of this solution will be equal to about .002 gramme iron, or nearly .001 gramme manganese, and if the permanganate is of the usual strength, say 1 c.c. = .007 gramme iron, 1 c.c. of the permanganate will equal about 3.5 c.c. of the ferrous sulphate. The permanganate solution having been carefully standardized, transfer 50 c.c. of the ferrous sulphate solution by means of a pipette to a dish, dilute to about 1 litre, and run in permanganate solution from a burette, stirring constantly until the first permanent pink tint appears. The reading of the burette will give the value of 50 c.c.

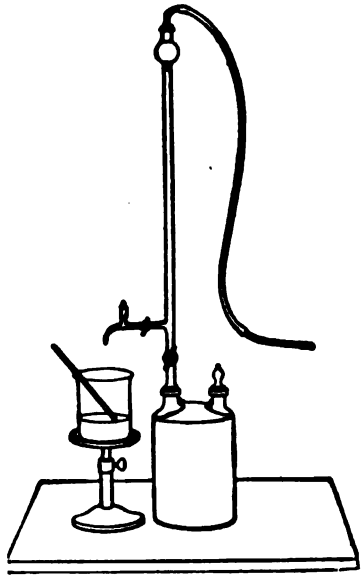
* Trans. Inst. Min. Engineers, x. 100.

† See page 51.

ferrous sulphate in permanganate, and consequently by a simple calculation its value in iron and manganese. Suppose, for instance, 1 c.c. permanganate solution = .0068 gramme iron, or (according to the proportion given above, 111.68 : 5493 :: iron : manganese) = .003345 gramme man- Then if 14.1 c.c. permanganate = 50 c.c. ferrous sulphate, 100 c.c. ferrous sulphate will be equivalent to 28.2 c.c. permanganate. In using oxalic acid, dissolve 2.25 grammes of the crystallized acid, $H_2C_2O_4$, $2H_2O$, in 1 litre of water, and determine its strength by pouring 50 c.c. into the dish, diluting with *hot* water, adding 5 c.c. sulphuric acid, and titrating with permanganate.

The details of the method are as follows: Weigh out 5 grammes of the sample of puddled iron, pig-iron, or steel, and proceed as directed on page 108 *et seq.;* but after filtering and washing the precipitated manganese dioxide with strong nitric acid, suck the precipitate as dry as possible, and then wash out the beaker in which the precipitation was made with cold water. Pour this water on the precipitate, and repeat the operation two or three times to get rid of all the nitric acid. Suck the precipitate as dry as possible, transfer it with the asbestos to the beaker in which the precipitation was made, measure into the beaker 100 c.c. of the standard ferrous sulphate solution (or 100 c.c. oxalic acid solution and 10 c.c. sulphuric acid), and stir until the manganese dioxide is all dissolved. When using oxalic acid it is necessary to heat gently to about 60° C. Wash the solution and asbestos into the dish, dilute to about 1 litre (with oxalic acid use hot water), and titrate with permanganate. We will suppose, for example, that it requires 10.2 c.c. permanganate to give the permanent rose tint; then, as 100 c.c. ferrous sulphate = 28.2 c.c. permanganate, there would be the equivalent of 28.2 — 10.2 = 18 c.c. permanganate in ferrous sulphate oxidized by the

FIG. 50.



manganese dioxide precipitate. One c.c. of permanganate being equivalent to .003345 gramme manganese, 18 c.c. = .06021 gramme manganese, and, 5 grammes of the sample having been taken, .06021 ÷ 5 = 0.01204 × 100 = 1.204 per cent. manganese.

Fig. 50 shows a very convenient piece of apparatus designed by Mr. E. A. Uehling in 1884.*

It is especially useful when it is necessary to add rapidly a constant volume of a standard reagent; for instance, a measured excess of ferrous sulphate in volumetric determination of manganese after precipitation with potassium chlorate.

The burette-tube extends to the bottom of the Wolff bottle, which holds 2 litres. Enough air is supplied, without danger of dust or evaporation of solution, by means of a pin-hole drilled in the neck of the bottle and through the hollow glass stopper. The bottle may be blackened to preserve the solution from the action of light.

Spiegel and Ferro-manganese

When working on spiegel or ferro-manganese, take .5 gramme of the sample and proceed in the same manner as directed for steel or iron; but it is better to use a standard solution of ferrous sulphate containing 30 grammes of $FeSO_4,7H_2O$ to the litre for very high ferro-manganese.

As there seems to be some uncertainty as to the exact composition of the manganese oxide,† the permanganate solution may be standardized as follows: Determine the absolute amount of manganese in a finely ground and well-mixed sample of spiegel or ferro-manganese by a gravimetric method, then treat .5 gramme of the same sample exactly as described above, and, having found the number of c.c. of permanganate that are equivalent to 100 c.c. of the ferrous sulphate solution, the amount of manganese in the sample divided by the number of c.c. of permanganate equivalent to the ferrous sulphate oxidized by the manganese oxide in the sample gives the value of the permanganate solution. Thus, if 100 c.c.

* Communicated to the author by Mr. A. L. Colby, of the Bethlehem Iron Company.

† Stone, Trans. Inst. Min. Engineers, xi. 323, xii. 295, 514; Mackintosh, Trans. Inst. Min. Engineers, xii. 79, xiii. 39.

ferrous sulphate solution require 28.2 c.c. permanganate to give the rose tint upon titration, the sample of spiegel contains 14.50 per cent. manganese, and the ferrous sulphate remaining after the solution of the manganese oxide in 100 c.c. requires 6.5 c.c. permanganate to give the rose tint upon titration (using .5 gramme of the sample, of which 1 gramme contains .1450 gramme manganese), the calculation would be as follows: 28.2 c.c. — 6.5 c.c. = 21.7 c.c. =.0725 gramme manganese, or 1 c.c. permanganate is equivalent to $\frac{.0725}{21.7}$ = .00334 gramme manganese.

Bismuthate Method

This method was originally proposed by Schneider,* and modified first by Reddrop and Ramage,† and then by Brearley and Ibbotson.‡

The method was based on the fact that a manganous salt in the presence of an excess of nitric acid is oxidized to permanganic acid by bismuth tetroxide. The permanganic acid formed is very stable in nitric acid of 1.135 sp. gr., when the solution is cold, but in hot solutions the excess of the bismuth tetroxide is rapidly decomposed, and then the nitric acid reacts with the permanganic acid, and, as soon as a small amount of manganous salt is formed, the remainder of the permanganic acid is decomposed, manganous nitrate dissolves, and manganese dioxide precipitates.

In the cold, however, the excess of the bismuth salt may be filtered off, and to the clear filtrate an excess of ferrous sulphate added, and the amount necessary to deoxidize the permanganic acid determined by titrating with permanganate. The end reactions are very sharp and the method is extremely accurate, but the presence of even traces of hydrochloric acid utterly vitiates the result. As pointed out by Reddrop and Ramage, bismuth tetroxide which was used by Schneider is difficult to obtain free from chlorides, and they recommended sodium bismuthate, which they prepare as directed on page 42.

The Method

Steels.—Dissolve 1 gramme of drillings in 50 c.c. of nitric acid (sp. gr. 1.135) in an Erlenmeyer flask of 200 c.c. capacity. Cool, and add about 0.5

* Ding. poly. J., 269, 224. † Trans. Chem. Soc., 1895, p. 268.

‡ "The Analysis of Steel Works Materials."

gramme of bismuthate. The bismuthate may be measured in a small spoon, and experience will soon enable the operator to judge of the amount with sufficient accuracy. Heat for a few minutes, or until the pink color has disappeared, with or without the precipitation of manganese dioxide.

FIG. 51.

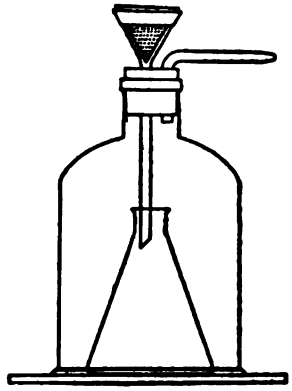
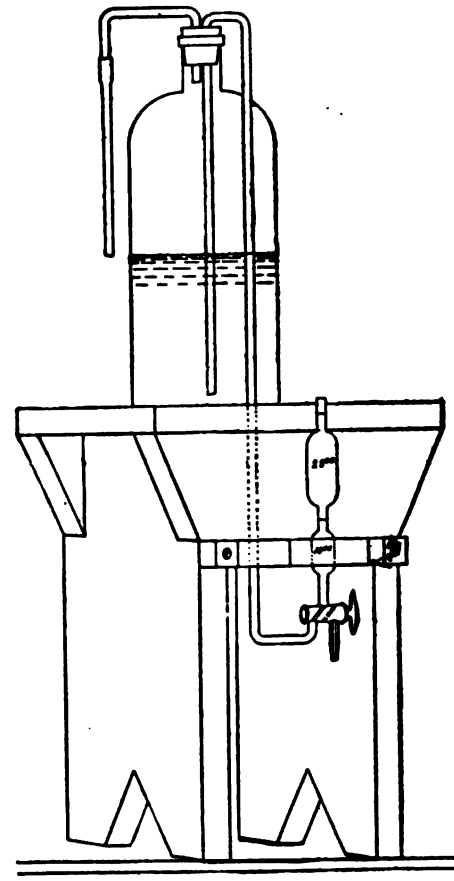


FIG. 52.



Add sulphurous acid, solution of ferrous sulphate, or sodium thiosulphate, in sufficient amount to clear the solution, and heat until all nitrous oxide has been driven off. Cool to about 15° C., add an excess of bismuthate, and agitate for a few minutes. Add 50 c.c. of water containing 30 c.c. of nitric acid to the litre, and filter through an asbestos felt on a platinum

cone * into a 300 c.c. Erlenmeyer flask and wash with 50 to 100 c.c. of the same acid. The arrangement shown in Fig. 51 has proved very satisfactory. Run into the flask from the pipette, shown in Fig. 52, a measured volume of ferrous sulphate solution and titrate to a faint pink color with permanganate. The number of cubic centimetres of the permanganate solution obtained, subtracted from the number corresponding to the volume of ferrous sulphate used, will give the volume of permanganate equivalent to the manganese in the sample, which, multiplied by the value of the permanganate in manganese, gives the amount of manganese in the steel.

Pig Iron.—Dissolve one gramme in 25 c.c. of nitric acid (sp. gr. 1.135) in a small beaker and, as soon as the action has ceased, filter on a 7 cm. filter into a 200 c.c. Erlenmeyer flask, wash with 30 c.c. of the same acid, and proceed as in the case of steels.

In the analysis of white irons it may be necessary to treat the solution several times with bismuthate to destroy the combined carbon. The solution, when cold, should be nearly colorless; if not, another treatment with bismuthate is necessary.

Iron Ores Containing less than 2 Per Cent. of Manganese.—Treat 1 gramme in a platinum dish or crucible with 4 c.c. of strong sulphuric acid, 10 c.c. of water, and 10 to 20 c.c. of hydrofluoric acid. Evaporate until the sulphuric acid fumes freely. Cool and dissolve in 25 c.c. of 1.135 nitric acid. If no appreciable residue remains, transfer to a 200 c.c. Erlenmeyer flask, using 25 c.c. of 1.135 nitric acid to rinse the dish or crucible, and proceed as usual. If there is an appreciable residue, filter on a small filter into a beaker, wash with water, burn the filter and residue in a crucible, and fuse with a small amount of potassium bisulphate. Dissolve in water, with the addition of a little nitric acid, add to the main filtrate, evaporate nearly to dryness, take up in 1.135 nitric acid, and transfer to the flask as before.

Manganese Ores and Iron Ores High in Manganese.—Fuse 1 gramme of the ore in a large platinum crucible with 20 grammes of potassium bisulphate. Heat very slowly and carefully until the water and gases are expelled and then raise the heat until the fusion is tranquil and the ore thoroughly decomposed. Dissolve the fused mass in hot

* Or on the alundum plate described on page 25.

water containing about 10 c.c. strong sulphuric acid and boil. If the decomposition is complete nothing will remain except a white precipitate, generally barium sulphate, but occasionally a small flocculent precipitate of manganese dioxide is present. The addition of a drop or two of sulphurous acid clears the solution instantly. Transfer the solution to a carefully calibrated litre flask and when the solution is at the temperature of the room make up to the mark with water. Mix thoroughly by pouring the solution into a large beaker and back into the flask twice.

Measure into a 200 c.c. Erlenmeyer flask such a volume of the solution as will contain from 10 to 20 milligrammes of manganese and add such amounts of strong nitric acid and water as will yield a mixture containing one part of nitric acid sp. gr. 1.4 to three parts of solution in a total volume of 75 to 80 c.c.. For example, in a 50 per cent. ore use 20 c.c. of the solution, 20 c.c. nitric acid, and 40 c.c. water.

In this case, the manganese must be calculated on $\frac{1}{50}$ of a gramme or 20 mg. of ore. When working on such amounts it is always desirable to make duplicate analyses and take the mean, as a difference of 0.1 c.c. makes a large error in the result. When the ore contains a much smaller amount of manganese, say 5 or 10 per cent., it is better to make up the solution to say 100 c.c. instead of a litre.

Special Steels.—Steels containing chromium offer no special difficulties, except that it must be noted that while in hot solutions the chromium is oxidized to chromic acid, which is reduced by the addition of sulphurous acid, the oxidation proceeds so slowly in cold solutions that if there is no delay in the filtration * and titration the results are not affected. Steels containing tungsten are sometimes troublesome on account of the necessity for getting rid of the tungstic acid. Those that decompose readily in nitric acid may be filtered and the filtrate treated like pig iron, but when it is necessary to use hydrochloric acid it is best to treat with *aqua regia*, evaporate to dryness, redissolve in hydrochloric acid, add a few drops of nitric acid, dilute, boil, and filter. Get rid of every trace of hydrochloric acid by repeated evaporations with nitric acid, and proceed as with an ordinary steel, or proceed as under Special Steels.

* 1½ minutes for the oxidation and about the same time for the filtration.

Reagents

Nitric Acid (sp. gr. 1.135).—A mixture of 3 parts of water and 1 part strong nitric acid answers perfectly for this purpose.

Nitric Acid (3 per cent.).—Thirty c.c. of strong nitric acid to the litre.

Permanganate Solution and Ferrous Sulphate Solution.—One gramme of potassium permanganate to the litre gives a solution of convenient strength, and 12.4 grammes of ferrous ammonium sulphate and 50 c.c. of strong sulphuric acid,* made up to 1 litre, give a solution which is almost exactly equal to the permanganate solution. As the strength of the ferrous sulphate solution changes quite rapidly, while the permanganate remains unaltered for months, it is unnecessary and troublesome to keep them of the same strength. By using a constant volume of the ferrous sulphate solution and testing it against the permanganate solution every day, the calculation of the results is very simple. It is necessary that the conditions should be the same in getting the strength of the ferrous sulphate solution as in titrating a solution for manganese, and after many experiments the following method of procedure was adopted: Measure into a 200 c.c. flask 50 c.c. of nitric acid (sp. gr. 1.135), cool, and add a very small amount of bismuthate, dilute with 50 c.c. of 3 per cent. nitric acid, filter into a 300 c.c. flask, and wash with 50 c.c. of 3 per cent. nitric acid. If the felt is well coated with bismuthate it is unnecessary to add any to the nitric acid in the flask, as filtration through the mass of bismuthate on the felt will answer the purpose. Run in from the pipette (Fig. 52) 25 c.c. of ferrous sulphate solution and titrate with the permanganate to a faint pink. This gives the value in permanganate of the ferrous sulphate solution. With this method of procedure the discrepancies that had occurred entirely disappeared, and it is possible to make any number of determinations with a variation of less than 0.1 c.c.

The permanganate solution is standardized exactly as described on page 90, where the method is given for determining the value of the permanganate solution used in the determination of phosphorus. As this solution is just half the strength of that used in the method for

* Dr. C. B. Dudley proposes to use 25 c.c. of sulphuric and 25 c.c. of strong phosphoric acid as tending to give a more nearly colorless solution.

phosphorus 0.1 gramme of oxalate is taken and requires about 47.5 c.c. of the permanganate. Multiply the weight of oxalate by 0.16397 and divide by the number of c.c. of permanganate necessary to get the pink color and the result is the value of 1 c.c. of the permanganate in manganese.

There was at one time a question as to the best reagent to use for standardizing the permanganate for use in this method. There seemed to be a difference in the results obtained by the use of iron wire or sodium oxalate and manganese sulphate, but Blum * showed conculsively that the difference was due to the extreme difficulty of getting an absolutely anhydrous manganese sulphate. When this was obtained the differences disappeared. The non-hygroscopic quality of sodium oxalate, its purity and permanence make it an ideal reagent for standardizing solutions of potassium permanganate.

Notes and Precautions

The delicacy of the reaction of manganese in nitric acid solution with sodium bismuthate is extraordinary,—0.000005 gramme of manganese gave an appreciable color in 50 c.c. of solution.

When the proper precautions are observed, this method for materials containing small amounts of manganese, say up to 2 per cent., is more accurate than any other method, volumetric or gravimetric, that I have ever used.

As will be seen in the description of the various methods of solution, the use of hydrochloric acid has been avoided, because the presence of even traces of this reagent is fatal to the accuracy of the method. Where it is impossible to avoid its use, and its presence is suspected in the final nitric acid solution, the addition of a drop or two of silver nitrate will overcome the difficulty, but the filter must be rejected after using it for filtering a solution so treated.

Any form of asbestos filtering tube may be used for filtering off the bismuthate, but the perforated cone or alundum plate with bell jar, shown in Fig. 51, is the most satisfactory, because it has the largest area of filtering surface. One filter may be used for ten or more determinations, and the time occupied in filtering and washing one determination

* Am. Chem. Soc. 34, p. 1388; 1912.

is only from one minute and a half to three minutes. The filtrate must be perfectly clear, for the least particle of bismuthate carried through will vitiate the result by reacting with the excess of ferrous sulphate. As soon as the filtration and washing are completed, the ferrous sulphate should be added and the excess titrated with the permanganate solution, as the permanganic acid gradually decomposes on standing, and the warmer the solution the more rapid is the decomposition. At a temperature of 5° C. the solution will remain unaltered for several hours, but at 40° C. fifteen minutes will show an appreciable change. The larger the amount of manganese the more rapid the change. It is especially important not to allow the solution to stand after adding the ferrous sulphate, as the excess of this reagent reacts with the nitric acid in a few minutes and the formation of the smallest amount of nitrous oxide is fatal to the accuracy of the determination. For this reason it is important to boil off every trace of nitrous oxide when, in the earlier part of the operation, sulphurous acid or other deoxidizing agent is added.

When working with steels of unknown manganese content, it may often happen that 25 c.c. of ferrous sulphate solution are insufficient to entirely reduce the permanganic acid, in which case an additional amount of ferrous sulphate must be added, and the pipette shown in Fig. 52 has been arranged to meet this contingency. It will be noticed that the solution of permanganic acid upon the addition of an insufficient amount of ferrous sulphate does not necessarily retain its pink or purple color, but usually changes to a dirty brown. When this occurs, the lower part of the pipette may be emptied directly into the flask and the value of the two parts taken as the amount from which the number of cubic centimetres of permanganate, corresponding to the excess of ferrous sulphate, must be subtracted. When the sample is low in manganese, the 10 c.c. portion of the pipette alone may be used, so that the arrangement allows a great deal of variation in the manganese content of the samples worked on.

There is no advantage in using permanganate solutions differing in strength from the one given above, but the strength of the ferrous sulphate solution may be changed to meet special cases.

I am surprised that this method has not come into general use, for it combines, in a remarkable degree, extreme accuracy and great rapidity with simplicity and ease of manipulation.

Deshays's Method

This method is based on the fact that manganese nitrate when boiled with excess of nitric acid and lead peroxide is oxidized to permanganic acid, which is reduced again by a standard solution of sodium arsenite.

Dissolve 0.5 gramme of steel or pig-iron in 30 c.c. nitric acid (1.2 sp. gr.) and boil until all reactions cease. Add cautiously 1 to 3 grammes lead peroxide or red lead and dilute with hot water to about 60 c.c. Heat the solution to boiling and allow the lead salt to settle. Decant the solution and boil the residue with 50 c.c. of nitric acid (1.13 sp. gr.). Decant as before and repeat the operation until the supernatant liquid is colorless. Filter the decanted liquid through asbestos and titrate with a standard solution of sodium arsenite. To prepare the standard solution, dissolve 4.96 grammes of arsenious acid together with 25 grammes of sodium carbonate in water and dilute to 2500 c.c. Dissolve 0.5 grammes of a steel containing a known amount of manganese in 30 c.c. nitric acid (1.2 sp. gr.) and treat it exactly as described above and divide the percentage of manganese by the number of c.c. of the standard solution required to decolorize the permanganic acid. This will give the value of each c.c. of the standard solution in manganese. For steels containing over 0.5% manganese use 0.25 gramme, and for those containing over 1.0% use only 0.1 gramme. Hot solutions of nitric acid decompose permanganic acid unless the permanganic acid is very dilute, for which reason it is necessary to use decreasing amounts of the steel as the manganese contents increase.

The Color Method (for Steel)

This method was first suggested by Pichard,* and was used essentially in its present form by Peters.† It requires one or more standard steels in which the manganese has been most carefully determined by a gravimetric method. When a number of samples are to be tested at the same time, as is usually the case, a bath like the one shown in Fig. 80 is necessary, but for the manganese color method it should contain a solution of calcium chloride, which boils at 115° C.‡ It is, of course, very necessary in a

* Comptes-Rendus Hebd. des Séances de l'Acad. des Sciences, December 30, 1872.

† Chem. News, xxxiii. 35. ‡ This latter modification is due to Mr. S. A. Ford.

method of this kind that the operations should always be conducted as nearly as possible under the same conditions, and that the standard should always be dissolved at the same time as the samples to be tested. Weigh .2 gramme of each sample of the standard, and place them in 8-inch test-tubes properly numbered. Pour into each test-tube 15 c.c. nitric acid (1.2 sp. gr.), cover each with a small glass bulb or very small funnel, and stand the test-tubes in the holes in the top of the bath, as shown in the sketch, Fig. 80. Heat in the bath at 100° C. until solution is complete. Pour the contents of a test-tube into a 100 c.c. tube, wash out the test-tube with cold water, adding it to the solution in the 100 c.c. tube, and finally dilute to the 100 c.c. mark. Mix thoroughly by placing the thumb over the top of the tube and turning it upside down several times. Draw out 10 c.c. of this solution with a pipette graduated to deliver 10 c.c., and let it run into the test-tube in which the solution was made. Treat each sample in this way, including the standard. The tube is merely washed out with water, but the pipette can best be cleaned by drawing it full from the 100 c.c. tube of the fresh sample, throwing the contents away, and filling it a second time to deliver into the test-tube. Stand the test-tubes in the rack again, add to each 3 c.c. nitric acid (1.2 sp. gr.), replace the bulbs or funnels, and stand the rack in the calcium chloride bath, the solution in which should now be boiling. When the *solutions in the test-tubes* begin to boil, add to each .5 gramme fine lead peroxide * and boil exactly five minutes. The lead peroxide can readily be measured by a small platinum spoon, made to hold about .5 gramme. It is necessary that the solutions in the test-tubes should boil, and it is easy to assure one's self of this fact by looking down into the test-tubes after the action caused by the addition of the lead peroxide has ceased. Remove the rack from the bath at the expiration of the five minutes, and stand it with the test-tubes in cold water to cool the solutions and allow the insoluble lead salt to settle. The insoluble matter settles to the bottom of the tube in a heavy compact mass, leaving the supernatant fluid perfectly clean. When this occurs, which is usually within the space of half an hour, the solutions are ready to be decanted into the comparison-tubes.† In working on a number of steels we will suppose that we use

* See page 53.

† See Fig. 82.

two standards, one containing 1.2 per cent. of manganese, the other 0.6 per cent. As we weighed out .2 gramme, diluted the solution to 100 c.c. and took 10 c.c. in which to determine manganese, the amount taken corresponds to .02 gramme of the sample; and if we dilute the solutions of the standards after decanting into the comparison-tubes to 24 c.c., 1 c.c. will correspond to 0.05 per cent. in the high, and 0.025 per cent. in the low, standard. Decant each solution in turn into a comparison-tube, and dilute it until it has the exact tint and depth of color of the standard to which it most nearly approximates when first decanted. The percentage of manganese is found by multiplying the number of c.c. to which the sample has been diluted by 0.05 or 0.025, according to the standard with which it has been compared. If, however, the solution of a sample when first decanted and before dilution should be lighter in color than the lower standard, the latter may, after the other samples have all been finished, be diluted to 30 c.c., when each c.c. will correspond to 0.02 per cent. manganese, or, if this color is not sufficiently light, to 40 c.c., when each c.c. will correspond to 0.015 per cent. manganese. When even this color is not sufficiently light, a lower standard must be used for comparison, or a larger amount of the sample taken for solution. The comparison of the colors should be made in a camera or box, as shown in Fig. 83.

The direct rays of the sun should not be allowed to shine on the solutions, and a northern light for the comparisons is preferable to any other.

Walters's Modification *

Taking advantage of Dr. Marshall's suggestions in the *Chemical News*, vol. lxxxiii. p. 76, Mr. Walters has elaborated a method which avoids the necessity for filtration and for the use of a calcium chloride bath and allows the colors of the solutions to be compared as soon as they are cool. It is based on the fact that when a solution of a steel in nitric acid is heated with ammonium persulphate in the presence of a small amount of silver nitrate the manganese is oxidized to permanganic acid. Dissolve .2 gramme of the sample and the same amount of a standard steel in test-tubes, using 10 c.c. of nitric acid 1.2 sp. gr. for each. Heat in water-bath

* Harry E. Walters in Proceedings of Engineers' Society of Western Pennsylvania, October, 1901.

until solution is complete and all nitrous fumes are driven off. Add to each 15 c.c. of a solution of silver nitrate (1.33 grammes to 1 litre), equal to .02 gramme $AgNO_3$. Then add immediately about 1 gramme ammonium persulphate, and continue heating the solution for about half a minute after the oxidation begins. Place the tube in cold water, and when cold compare as usual.

In the case of steels containing upward of 0.75 per cent. manganese use only .1 gramme. If the ammonium persulphate looks very dry, it should be moistened slightly a day or two before using; 10 c.c. of water to a pound of the salt is sufficient.

For pig-iron dissolve 1 gramme in a small beaker in 30 c.c. nitric acid 1.2 sp. gr. on the hot plate. Filter into a 100 c.c. calibrated flask and dilute to the mark. Mix well and pour 20 c.c. (10 c.c. if high in manganese) into a test-tube, warm, and add a little ammonium persulphate to destroy the combined carbon and give a clear solution. Add 5 c.c. silver nitrate solution (1 gramme of the salt to 250 c.c. water), add a little more ammonium persulphate, and proceed as before.

DETERMINATION OF CARBON

Carbon differs from all other elements in iron and steel in that it is supposed to exist in several conditions, and analytical chemistry supplies the means of distinguishing between at least two of these conditions. Until within a few years it was considered to exist in two forms, as graphite and as combined carbon. To Karsten is due the recognition of the fact that graphite is a form of pure carbon, and not a compound of carbon and hydrogen. It is always present as a mechanical mixture, and is thus distinguished from the other form, which was supposed to be combined chemically with the iron. Of late years the opinion has been growing that "combined carbon" exists in at least two conditions in steel, but as yet chemical methods for separating and distinguishing between these conditions have failed, so far as quantitative work is concerned. The analytical methods here given are:

The Determination of Total Carbon,
The Determination of Graphitic Carbon, and
The Determination of Combined Carbon.

DETERMINATION OF TOTAL CARBON

We may divide the methods for the determination of total carbon in iron and steel into the following classes:

A. The direct treatment of the borings or drillings without previous separation of the iron, including:

1. Direct combustion in a current of oxygen.

2. Direct combustion in a Gooch tubulated crucible.

3. Direct combustion in current of oxygen and absorption in barium hydroxide.

4. Combustion with lead chromate and potassium chlorate (Regnault).

5. Combustion with cupric oxide in a current of oxygen (Kudernatsch).

B. Removal of the iron by volatilization, and subsequent combustion of the carbon, including:

1. Volatilization in a current of chlorine (Berzelius, Wöhler).

2. Volatilization in a current of hydrochloric acid gas (Deville).

C. Solution of the iron, and combustion or weighing of the residue, including:

1. Solution in potassium-cupric chloride, filtration, and combustion of the residue in oxygen (Richter).

(*a*) Combustion of residue with sulphuric and chromic acids.

(*b*) The Shimer crucible for combustion in air or oxygen.

2. Solution of the iron in cupric sulphate, filtration, and combustion of the residue in a boat in a current of oxygen (Langley).

3. Solution of the iron in cupric sulphate, and oxidation of the residue by chromic and sulphuric acids (Ullgren).

A. 1. Direct Combustion in a Current of Oxygen

The thorough combustion of steel drillings and subsequent complete oxidation of the contained carbon is merely a question of temperature. At one time I was firmly convinced that at a temperature slightly above a dark red, platinum was permeable by carbon monoxide and dioxide and that it was, therefore, dangerous to heat a platinum tube above this point in the determination of carbon. Exhaustive experiments have convinced me of the fallacy of this assumption. With the proper treatment, any

ordinary drillings may be completely burned, and it is unnecessary to have the steel in any finer state of subdivision than is requisite for obtaining a proper average of the sample. These results apply not only to ordinary steels and pig iron, but experiments have shown conclusively that with chrome-tungsten steels the direct method is the only one capable of giving accurate results, those obtained by solution in potassium-cupric chloride being invariably from 10 per cent. to 40 per cent. too low.

There are two possible sources of error in this method which should be guarded against. A part of the carbon is undoubtedly given off as carbon monoxide, and therefore the space occupied by the platinum gauze or fine wire in the combustion tube should contain enough oxygen to completely oxidize the carbon monoxide to dioxide. This may be accomplished in the case of steels or irons containing over 1.5 per cent. carbon by using the half factor weight, or even as little as 1 gramme of the sample. This source of error does not exist when cupric oxide is used, but in this case cupric sulphate forms and is gradually decomposed, liberating sulphurous acid, which unless provided for will pass into the absorption apparatus and thus increase the apparent amount of carbon in the sample.

The second source of error lies in the presence of sulphur in the sample. This is oxidized largely to sulphuric, but sometimes only to sulphurous acid. To fully oxidize the latter, I have substituted for the tube C a potash bulb of the form known as Geissler's in which the products of combustion bubble through three small bulbs containing a saturated solution of chromic acid. The contents of this tube must be changed as soon as the chromic acid in the second bulb begins to darken.

The sulphuric anhydride will often pass through these bulbs and must be condensed and held in tube D containing anhydrous cupric sulphate. When burning a high sulphur steel, if the gas is passed too rapidly through the apparatus, the sulphuric acid will liberate hydrochloric acid from the calcium chloride, which will pass into the absorption apparatus and vitiate the result.

The ignited alumina which was used successfully for some years to line the boat in which the drillings were placed, became so impure, either from some change in method of manufacture or from carelessness, that it had to be abandoned. After trying several substances it was

found that alundum, 120 mesh, manufactured by the Norton Company, answered every requirement. It is free from carbonic acid and other impurities, and allows the steel to be perfectly oxidized without melting into globules and thus occluding unoxidized particles of the metal. As alundum by itself has no adhesive quality, it should be prepared by mixing with it a little clay, free from carbonates (about 1 gramme clay to 100 grammes alundum) and moistening slightly. When pressed into the boat in this condition, it keeps its shape and after ignition drillings can be placed in the depression without sinking into the alundum, and the oxide of iron formed during the combustion has little tendency to go through the alundum and stick to the bottom of the boat.

The oxygen now furnished in special cylinders is so pure and free from oil or other organic matter that a preheater is unnecessary, and by using a reducing valve the second cylinder may be dispensed with. Pig-iron borings may be perfectly burned in the boat, but a half factor weight only should be taken.

FIG. 53.

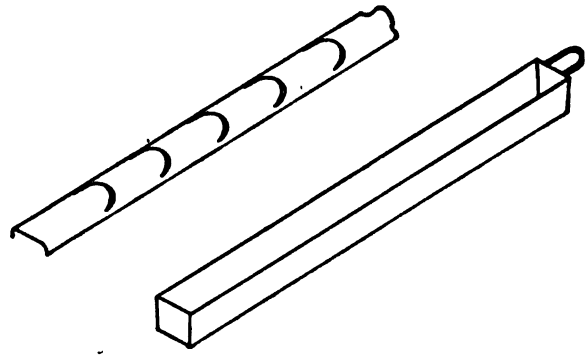
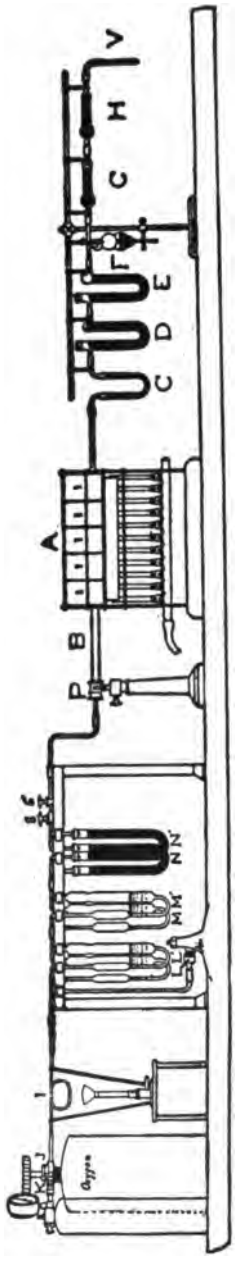


Fig. 53 shows the boat and cover used in this method. The boat is 6 inches (150 mm.) long, ⅜ inch (9 mm.) high, and ½ inch (12 mm. wide on top and slightly narrower on the bottom. The cover fits loosely on the boat, and is provided with several openings formed by making semicircular cuts at intervals and slightly raising the edges. The openings serve to admit the oxygen freely, while the cover prevents the particles of oxide of iron thrown off the steel during the combustion from reaching the inside of the tube.

FIG. 54.



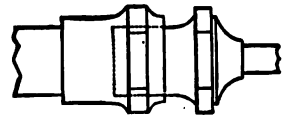
Fill the boat with ignited alundum and make a V-shaped depression in the middle with a spatula, pressing the material against the sides of the boat. Adjust the cover and ignite the boat and its contents strongly, to expel any carbon dioxide present and to oxidize any carbonaceous matter that the alundum may contain.

Weigh a factor weight (2.7273 grammes) of the drillings and transfer it to the boat, being careful to distribute the material evenly in the depression without allowing any of the particles to be in contact with the platinum.

The general arrangement of the combustion apparatus is shown in Fig. 54. It consists of a platinum tube, B, 24 inches (600 mm.) long and ⅝ inch (16 mm.) in diameter from the joint P to the forward end of the furnace A, where it is contracted for a length of 6 inches (150 mm.) to a diameter of ¼ inch (6 mm.). The rear end has a ground joint P, which is made perfectly air tight. The details of the joint are shown in Fig. 55.

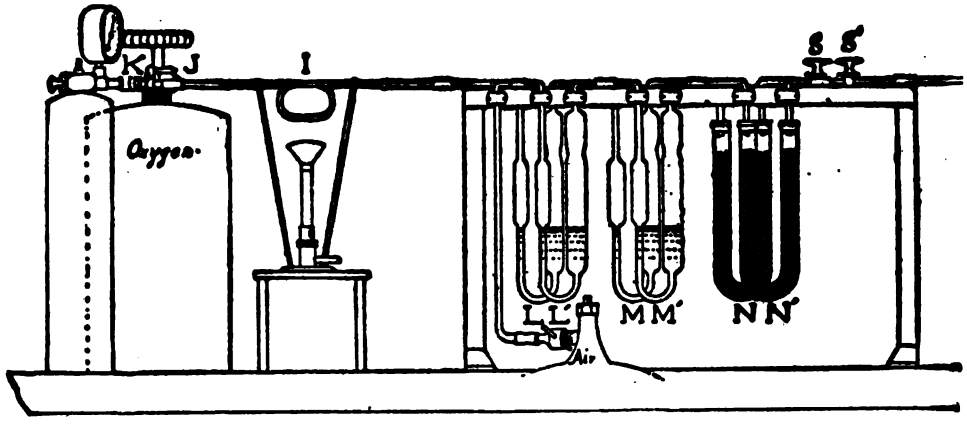
The tube has a strengthening band of German silver, and the plug through which a platinum tube 4 inches (100 mm.) long and ¼ inch (6 mm.) in diameter passes is made of phosphor-bronze. The forward end inside the furnace contains a plug of loosely wound platinum gauze 5½ inches (138 mm.) long, completely filling the bore of the tube, and a similar roll 2 inches (50 mm.) long fitted with a loop is pushed in after the boat. The rear end of the tube at the joint may be supported by

FIG. 55.



a wire from above or by a stand as shown in the sketch, Fig. 54. The small U-tube C is filled with glass beads moistened with chromic acid solution, with a loose plug of glass wool in the forward end. This serves to oxidize any sulphurous anhydride and to absorb the sulphuric anhydride formed from the sulphur in the steel during the combustion. This tube is washed out daily and fresh glass wool inserted. The U-tube D contains pieces of anhydrous cupric sulphate, and E, dried granulated calcium chloride. The purifying apparatus for oxygen and air is shown in Fig. 56.

FIG. 56.

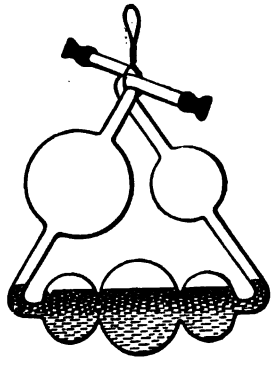


Oxygen from the large cylinder is passed into the smaller one until the pressure is from 150 to 200 pounds to the square inch, when the larger cylinder is closed and the gas is passed from the smaller cylinder through the apparatus, it having been found difficult to regulate the flow of gas properly by means of the valve in the large cylinder which is adapted to the heavy pressure of gas contained in these cylinders. While filling the smaller cylinder the stopcock K is closed, and when the valves in both cylinders are shut the pressure is relieved by opening this stopcock after disconnecting the rubber joint J. The preheating tube I is of platinum with glass fused on each end and contains fine platinum wire in the loop. It serves to burn any hydrocarbon that the oxygen may contain. The tubes L and L′ and M and M′ contain potassium hydrate (1.27 sp. gr.). The U-tubes N and N′ contain fused potassium hydroxide. The oxygen

passes through the tubes L, M, and N and the stopcock S, the air through L′, M′, and N′ and the stopcock S′. A Y-tube connects the two, and the gas or air passes through the glass tubes connected by rubber joints into the combustion-tube.

The absorption apparatus consists of the Liebig bulb F and the drying tube G, Fig. 54. F contains solution of potassium hydrate (1.27 sp. gr.). It is filled by attaching a short piece of rubber tubing to one end and applying suction to it, the other end being immersed in the potassium hydrate solution contained in a beaker or dish. The end must be wiped dry with a little filter-paper and the inside of the tube dried in the same way. When filled, the bulb should contain the solution as shown in Fig. 57. When attached to the apparatus, the gas passes first into the large bulb, and, the bulbs being inclined, the gas bubbles through the solution in the three bottom bulbs. It is fitted with a loop of platinum wire, as shown in Fig. 57.

FIG. 57.

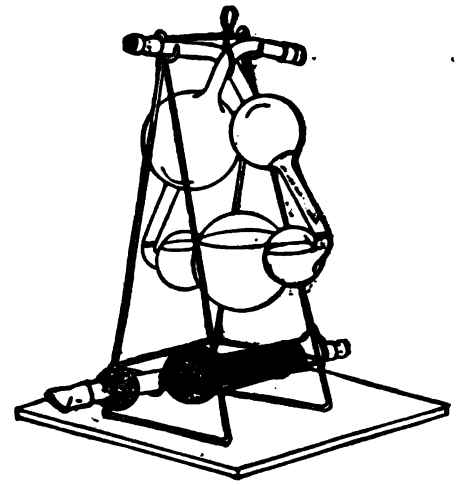


The drying tube contains dried calcium chloride. The small bulb of the drying tube, Fig. 58, contains a plug of cotton-wool, and another plug of the same material is inserted after the calcium chloride. H is a safety-guard tube, to prevent moisture from getting into the tube G during the combustion. The short rubber tube V is used to draw a little air through to test the tightness of the joints. All the stoppers in the various U tubes and drying tubes are of rubber. A copper rod is used to introduce the boats, etc., into the tube B. When not attached to the apparatus, the ends of the potash-bulb F and drying tube G are closed by little caps of rubber tubing (Fig. 57) made like the tips for "policemen." When on the balance, however, they should be closed with short pieces of rubber tubing containing bits of capillary glass tubing, as shown in Fig. 58. The forward end of the drying tube is closed in the same way. These openings are too small to allow the condition of the atmosphere to affect the weight of the bulbs by loss or gain of moisture, but they serve to equalize the pressure and make it unnecessary to reopen the balance case until the bulbs are weighed.

It is very necessary in filling the potash-bulb to avoid getting any of the

solution on the outside of the bulb, and it is well to see that both the bulb-tube and the drying tube are perfectly clean. Wipe the potash-bulb and drying tube with a piece of linen, not silk (a clean linen handkerchief that does not leave lint on the glass is very good for this purpose), and place them on the balance.

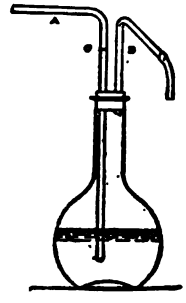
FIG. 58.



The little wire stand shown in Fig. 58 is very convenient for holding the absorption apparatus in the balance, as it brings all the weight on the pan, instead of putting the greater part on the beam alone, as is the case when the potash-bulbs are suspended from the hook on the end of the beam. Allow it to remain about thirty minutes to get the exact temperature of the balance, and weigh.

In the meantime turn on the oxygen after closing the stopcock S′ Fig. 54, heat the platinum tube to bright redness in the furnace, and, by means of a small blast lamp or Bunsen burner, heat the forward end to drive out any sulphuric acid that may remain in the tube. Turn out the burners of the furnace, turn off the oxygen, close the stopcock S, open S′ and start a slow current of air through the apparatus. When the tube is cool, attach the U-tubes C, D, and E, shut off the air, close the stopcock S′, and test the tightness of the connections by attaching a flask or bottle containing water and fitted with a cork carrying two glass tubes as shown in Fig. 59 to the forward end of E.

FIG. 59.



By drawing air through the tube B the water will rise in A, and if it keeps its level for a few minutes, we may be certain that all the connections are air tight. If it does not, the defective connection must be discovered and repaired. Open the rear end of the tube, insert the boat containing the drillings, and push it forward by means of a rod until it

is in contact with the gauze plug. Push the short plug in after it, close the tube, and attach the weighed absorption apparatus as shown in the sketch, Fig. 54. Start a slow current of oxygen through the apparatus and light the burner under the preheater and the first three or four burners under the forward end of the tube, and when the tube is red hot light the other burners in succession. As soon as the forward end of the boat gets hot the drillings begin to burn and the absorption of oxygen is very rapid. The valve controlling the supply of oxygen must be regulated so as to keep a slow current of gas passing through the absorption apparatus. It is not desirable to light the burners in very rapid succession, as under these circumstances the drillings burn very rapidly, and the heat generated by the combustion is so great that the oxide of iron melts, and, running through the alumina, fuses to the bottom of the boat, from which it is sometimes difficult to dislodge it. It may even in extreme cases run through the boat and pass to the tube itself. When all the burners are lighted and the absorption of oxygen has practically ceased, turn the burners up to the full extent and maintain the tube at the highest possible temperature for five minutes. Turn off the oxygen, turn on the air, extinguish the burners, and allow the air to pass for twenty or twenty-five minutes. Shut off the air, detach the absorption apparatus, and weigh it with the same precautions as before. The increase in weight is the carbonic acid from the carbon in the steel and contains 27.27 per cent. of carbon. When the factor weight is used for the combustion, each tenth of a milligramme increase of weight in the absorption apparatus is 0.001 per cent. carbon in the steel.

Notes and Precautions

Where current is available an electric furnace may be used instead of the gas furnace described in this method. It offers may advantages, the manipulation is simple, the requisite temperature is easily obtained and regulated, and either fused quartz, porcelain or platinum tubes may be used. In many laboratories the tube is not allowed to cool, but the forward end is kept hot and the operation is somewhat shortened in this way. Some chemists do not replace the oxygen in the absorption apparatus by air, but as soon as sufficient oxygen has been passed through to carry all the carbon dioxide into the absorption apparatus they detach,

close it with solid stoppers, and weigh it as soon as it has acquired the temperature of the balance. Of course the absorption apparatus must be filled with oxygen before the first weighing is made, so that the conditions may be the same for both weighings. Besides the one described, many forms of absorption apparatus are in use, in some of which soda lime is used instead of potassium hydroxide. In determining total carbon in pig-iron or cast-iron, the drillings should be moistened with alcohol, ground in a porcelain or Wedgwood mortar, transferred to a watch glass and carefully dried. The portion for analysis should be obtained by taking small portions from different parts of the sample without further mixing. In this way only can the proper proportion of graphite be secured. A half factor weight should be used. A diamond pointed drill with very slow speed should be used in taking samples of steel as this furnishes drillings of the best size and shape. They may be ground in a Wedgwood mortar, broken in a hardened steel mortar, or, if necessary, cut into small pieces with shears.

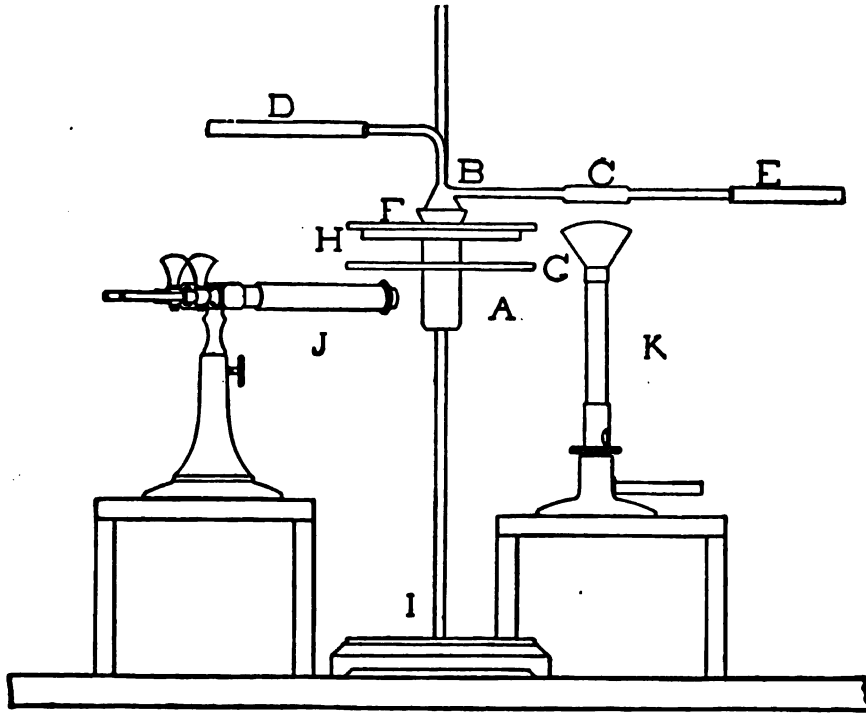
2. Direct Combustion in a Gooch Tubulated Crucible

Several modifications of the Shimer crucible have been proposed for the determination of carbon in steel and iron and most of them are available for direct combustion. A water-cooled rubber joint has its disadvantages, which are not found in the Gooch tubulated crucible, the details of which are shown in Fig. 94. The crucible used for the direct combustion of steel and iron differs in some of its details from the one shown in Fig. 94. The flange is deeper, the cap, while the conical part goes to the bottom of the flange, does not fit tightly, and the horizontal tube through which the products of combustion pass is much longer and widens out at the point C, Fig. 60, for a distance of an inch (25 mm.). This portion of the tube is filled with fine platinum wire or spongy platinum and heated by a burner to facilitate the oxidation of any sulphur dioxide or carbon monoxide that may be present.

As shown in the cut, Fig. 60, the apparatus consists of the crucible A, which is supported by a disk of asbestos board, F, cut to fit closely under the flange, resting on the ring H, attached to the upright of the stand I. A second disk of asbestos board, G, occupies the position shown in the cut

and is held in place by a piece of platinum wire encircling the crucible under the disk, which is heavy enough to keep its position and support the weight of the asbestos. This disk serves to prevent the heat from extending upward on the crucible and melting the sodium tungstate in the flanged joint. The pieces of glass tubing D and E are attached to the platinum by melting a little "sealing in" glass on the ends of the platinum tube and then fusing th ordinary soft glass tubing tc t.

FIG. 60.



The tube D is connected with the oxygen and air, and E to the tube C in the sketch, Fig. 54. The apparatus, therefore, takes the place of the platinum tube. Two ordinary crucibles, about 1½ inches (37 mm.) high and narrow enough to slip easily into the flanged crucible, should be provided.

Put enough alundum in the flanged crucible A to fill it to the depth of about ½ inch (12 mm.) and fill one of the small crucibles full of the same

material. With a pair of forceps put the small crucible in the large one and press it down well into the alundum. By means of the blast-lamp J heat the crucible to bright redness to destroy any carbonaceous matter and to drive off any carbonic acid that may be in the alundum. Cool, remove the small crucible, and with a glass rod press the alundum down to form a conical hole extending half-way to the bottom of the crucible. Weigh one gramme of the steel or iron drillings, transfer them carefully to the crucible, so that none of them may be in contact with the sides of the crucible, which should be perfectly covered by the alundum. Place the crucible in the large crucible A as before, put the cap B in place in the flanged joint, and connect the tube D with the tube from the oxygen and air supplies, Fig. 54. Fill the joint around the cap with small pieces of sodium tungstate, prepared by melting ordinary sodium tungstate in a platinum dish with one-tenth its weight of tungstic acid, and, when perfectly fused, running it over the bottom and sides of the dish and allowing it to cool in a thin layer. Fuse the sodium tungstate in the joint by a flame from the blast-lamp J, at the same time passing a rapid current of oxygen through the apparatus to prevent the carbonic acid of the flame from entering the tubulated crucible. Allow it to cool while the current still passes, then shut off the current, attach the tubes C, D, and E, Fig. 54, and test the tightness of the joints by means of the bottle, Fig. 59, as directed in the previous method. Attach the previously weighed absorption apparatus, light the burner K, Fig. 60, and start the oxygen through the apparatus. Heat the crucible A, Fig. 60, with the blast-lamp J in the position shown in the cut. The flame of the lamp should be large enough to surround the crucible and the full heat may be applied at once, the current of oxygen being so regulated as to keep up a constant current of three or four bubbles a second through the Liebig bulb F, Fig. 57. When the absorption of oxygen has ceased, turn off the oxygen, turn on the air, extinguish the blast-lamp J and the lamp K, and after the air has passed for fifteen or twenty minutes shut it off and detach and weigh the absorption apparatus. Detach the tube E, melt the sodium tungstate in the joint with the blast-lamp, and, holding the horizontal tube of the cap with a piece of asbestos board, withdraw the cap from the joint. Allow the edge to rest on the ring F, remove the small crucible, and replace it with another

crucible containing a weighed portion of drillings. Replace the cap in the joint, start a rapid current of oxygen, fuse the sodium tungstate, while fused press the cap down into the joint, allow it to cool, and proceed with the combustion.

3. Direct Combustion in a Current of Oxygen and Absorption in Barium Hydroxide

Instead of absorbing the carbon dioxide in potassium hydroxide it may be absorbed in a solution of barium hydroxide and the resulting barium carbonate may be filtered and weighed, or it may be dissolved in hydrochloric acid and the barium precipitated by sulphuric acid and weighed as barium sulphate. The barium carbonate may also be filtered and titrated against a standard acid. This method has been worked out by Dr. J. R. Cain.* The details are as follows:

Apparatus for Combustion

Apparatus.—The method requires no modification of any of the accepted appliances for the combustion of iron and steel. In the present work both gas and electrically heated furnaces were used. As already stated, there was no purifying train after the furnace, the Meyer tube being directly attached. Before the furnace was an electrically heated porcelain tube filled with copper oxide; then a calcium chloride tower filled with stick potassium hydroxide. Steels and irons were burned on a bed of alkali- and carbon-free alundum contained in a platinum boat. The blanks obtained by carrying through a complete determination, including filtration, washing, etc., but with omission of any carbon-containing substance, were usually 0.0 c.c. and never more than 0.05 c.c. of N/10 hydrochloric acid, showing not only that the oxygen was sufficiently purified and the apparatus in good condition, but that the operations of filtration, washing, etc., introduced no appreciable positive error.

Filtration and Washing of the Barium Carbonate.—This is carried out with the apparatus shown in the figure. The cut is approximately one-

* Journal of Industrial and Engineering Chemistry, Vol. vi, No. 6, page 465, June 1914.

tenth size and is self-explanatory. *S* is a two-way stopcock connected to the suction pipe. The rubber tubing connected to the Meyer tube should be of best grade black rubber, and the lengths used should be chosen so as to permit of easy manipulation of the tube. The Meyer tube is connected or disconnected by the rubber stoppers which are left always attached to the rubber tubes. The carbon filter *C* is fitted with a perforated porcelain plate, sliding easily. The funnel is prepared for filtrations by making a felt of asbestos on the porcelain disc, using asbestos which has been digested for several hours with strong hydrochloric acid and then washed free of acid. On top of the asbestos is placed a layer of similarly washed quartz of the height shown in the

FIG. 61.

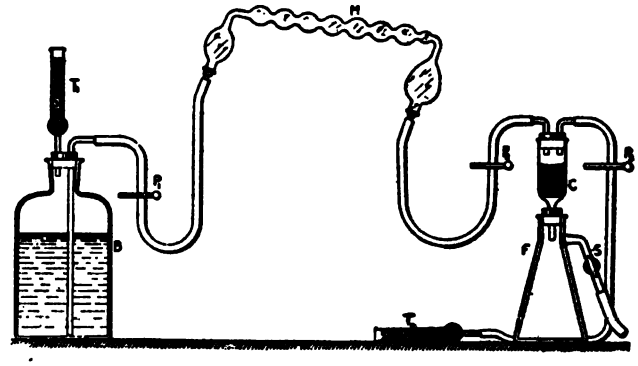


figure. A mixture of grains of various sizes (approximately 50 per cent. passing a 20-mesh and the remainder passing a 10-mesh and remaining on a 20-mesh sieve) is suitable. A mixture of quartz and asbestos works well and may be simply obtained by filling the funnel with a suspension of asbestos and delivering the quartz to the funnel from a beaker by means of a strong jet of water from the wash bottle, while maintaining a gentle suction. In this way the asbestos is properly mixed with the quartz. Proper attention to these details will be found to greatly expedite filtration. The stopper is now inserted in the funnel, the Meyer tube connected as shown, and the liquid and precipitate sucked into the funnel. Only very gentle suction should be used. When neces-

sary, *P*3 is opened to admit air back of the column of liquid in the Meyer tube. When the contents of the tube have all been transferred, the large bulb nearest *B* is half-filled with water by opening *P*1; the stopcock *S* is operated during this and subsequent operations so as to maintain a gentle suction. *M* is now manipulated so as to bring the wash water in contact with all parts of the interior, after which the water is sucked up through *C; P*2 is left open during this and subsequent washings. After eight washings, as directed, allowing the wash water to drain off thoroughly each time before adding more, *M* may be detached, the stopper removed from the funnel and the washing completed by filling *C* to the top with CO_2-free water, sucking off completely and repeating the operation once. Air is now admitted through the side opening of *S*, *C* is removed and the porcelain disc carrying the quartz asbestos and barium carbonate is shoved, by means of a long glass rod, into the flask used for titrations, removing from the sides of *C* any adhering particles by a jet of water from the wash bottle.

Solutions Used

Tenth-Normal Hydrochloric Acid.—Standardized by any of the accepted methods, or as follows: 20 c.c. of the approximately *N*/10 acid are measured out with a pipette, 5 c.c. of nitric acid (1 to 1 by volume) added, and the silver chloride precipitated by an excess of silver nitrate solution in a volume of 50 to 60 c.c. After digesting at 70° to 80° until the supernatant liquid is clear, the chloride is filtered off on a tared Gooch filter and washed with water containing 2 c.c. of nitric acid per 100 c.c. of water until freed from silver. After drying to constant weight at 130°, the increase of weight over the original tare is noted and the strength of the hydrochloric acid calculated on the basis of the weight of silver chloride thus obtained, afterwards adjusting to the strength prescribed. Several concordant determinations with varying amounts of acid should be made. 1 c.c. *N*/10 HCl = 0.0006 gramme carbon.

Tenth-Normal Sodium Hydroxide Solution.—Standardized against the hydrochloric acid solution, with methyl orange as indicator. This solution is conveniently stored in a large glass bottle fitted with a soda-lime guard tube and arranged for delivering the solution by air pressure.

Methyl Orange.—0.02 gramme dissolved in 100 c.c. of hot water and filtered.

Barium Hydroxide Solution.—A saturated solution filtered and stored in a large reservoir from which it is delivered by air pressure, protecting from carbon dioxide by a soda-lime tube. Three or four small bulbs of the Meyer tube are filled, and CO_2-free water is added until the remaining small bulbs are filled. When burning products high in carbon the stock solution may be used undiluted.

Carbon Dioxide-Free Water.—This is conveniently made by passing air for a sufficient length of time through a soda-lime tube and into a 6- or 8-litre bottle filled with pure distilled water. The water is delivered by CO_2-free air under pressure.

The Method

The combustion is carried out in the usual manner, care being taken not to pass the oxygen too rapidly. After filtering, washing and transferring the contents of the filter to a flask, as described under " Filtration and Washing of the Barium Carbonate," a slight excess of the standard acid is added from a burette, using a portion to rinse out the Meyer tube, and the excess of acid is then titrated against the sodium hydroxide, using methyl orange as indicator.

Notes and Precautions

1. After a little practice a precipitate can be filtered and prepared for titration in five minutes.

2. When working with steels high in carbon (above 1% it is advisable not to use more than one gramme, in order that filtration may be sufficiently rapid.

3. For very accurate work the Meyer tubes should be washed with dilute acid before beginning work each day. After a determination is finished, the Meyer tube should be completely filled two or three times with tap water, then rinsed with distilled water, in order to remove the carbon dioxide liberated when dissolving the carbonate from the previous determination.

4. The flask containing the carbonate should be very thoroughly agitated after adding the acid, since the carbonate sometimes dissolves rather slowly if this is not done; this is particularly the case if it has packed much during filtration.

5. The rubber tube connecting *B* (see figure) to the Meyer tube should be washed with a little water from *B*, before beginning determinations each day.

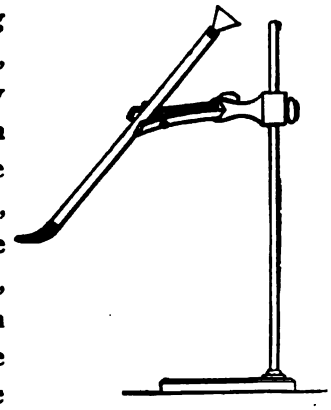
4. Combustion with Lead Chromate and Potassium Chlorate

This method requires the sample to be very finely powdered. Take a piece of combustion-tubing about 32 inches (800 mm.) long, ½ inch (12 mm.) internal diameter, $\frac{1}{16}$ inch (1.5 mm.) thick in the walls; heat it in the middle by means of a blast-lamp until it softens, draw the ends apart slightly, and then, keeping the ends parallel, draw it out as shown in Fig. 62. Allow it to cool, scratch it in the middle with a file, and break it. This gives two tubes, each about 16 inches (400 mm.) long. Fuse the large ends slightly so as to round the sharp edges, but avoid contracting the tube. Wash the tubes thoroughly, using a rod with a piece of dark-colored silk or linen on the end; then if any lint remains on the inside of the tube it can easily be seen. Dry the tubes by heating them carefully and drawing air through them, then fuse the small ends and cork the large ends to keep out the dust. Weigh carefully from 1 to 3 grammes (1 gramme of pig-iron, spiegel, or ferro-manganese, 3 grammes of steel) of the sample, and grind it thoroughly in a small mortar with 15 times its weight of fused and powdered lead chromate and 1½ times it weight of fused and powdered potassium chlorate or potassium bichromate. Potassium bichromate is to be preferred, as a little chlorine is sometimes given off by potassium chlorate when used in this manner. Place the combustion-tube in a stand, as shown in Fig. 63, and push down into the end, with a clean glass rod, a little ignited asbestos. The asbestos should not be tightly packed, as it will prevent the air from passing in

FIG. 62.

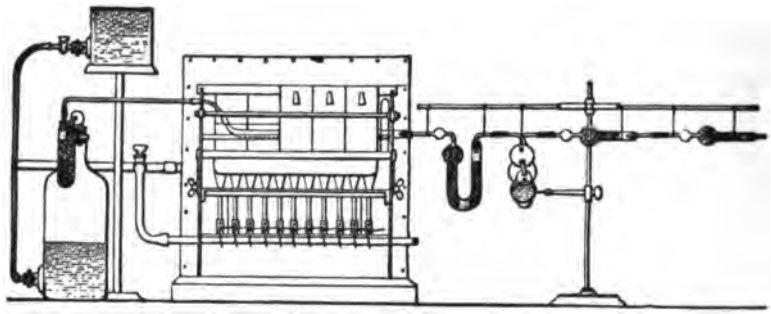
freely at the end of the operation. Place a small, dry, perfectly clean funnel in the end of the tube, and pour through it enough of the pure powdered lead chromate to fill the tube for about one inch of its length. Hold the mortar under the funnel so that anything that falls from it may go into the mortar, and charge the mixture into the tube by means of a small platinum spatula. Clean out the mortar by grinding in it two or three successive small portions of lead chromate, charging each into the tube through the funnel. Remove the funnel, cork the tube, and, holding it in a horizontal position with the tail up, tap it gently to get a clear space for the passage of the gas from one end of the tube to the other. Place the tube in the combustion-furnace, remove the cork, and insert in its place a smooth velvet cork, through the centre of which passes one end of a Marchand U-tube. The half of this tube nearest the combustion-tube contains anhydrous cupric sulphate, and the other half granulated dried calcium chloride, the two reagents being separated by a small plug of fibrous asbestos loosely packed. Weigh, and attach the absorption apparatus and safety-tube. Apply suction at the end of the rubber tube on the forward end of the safety-tube, and draw a few bubbles of air through the potash-bulb. Allow the liquid to recede gradually; if it maintains its level in the bulb for a few minutes, the joints of the apparatus may be considered tight, but if it gradually falls, it is proof that there is a leak, and the joints must all be tightened. If, after pushing the cork as far as possible into the end of the combustion-tube and binding all the rubber connections, another trial still shows a leak, a fresh cork must be substituted. When the joints are all tight, light the burner at the forward end of the tube, and each burner successively as the flow of gas slackens, bringing the tube over each burner to a red heat before lighting the next one. Maintain the whole length of the tube up to the asbestos at a good red heat until the flow of gas entirely ceases. Then pass a piece of rubber tubing

FIG. 63.



attached to a purifying apparatus well over the tail of the tube, which should be cool enough to be handled, break the point of the tail inside the tubing, lower the lights a little, and, by means of the aspirator-bottles, force about 1 litre of air through the apparatus. It will now appear as in Fig. 64. Turn out the lights, and detach and weigh the absorption

FIG. 64.

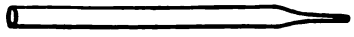


apparatus, with the precautions mentioned on page 133. The increase of weight will be the carbonic acid due to the carbon in the sample. This contains 27.27 per cent. carbon.

5. Combustion with Cupric Oxide in a Current of Oxygen

Prepare the combustion-tube as directed in the last method, and pour on the asbestos in the end of the tube enough cupric oxide to fill the tube to the height of about an inch (25 mm.). Mix the weighed sample—from 1 to 3 grammes in a fine state of division—with at least twenty times its weight of finely-powdered pure cupric oxide, charge it into the tube as directed on page 142, rinse out the mortar with a little more of the same material, and finally fill the tube to within an inch (25 mm.) of the end with granulated cupric oxide. Make the combustion exactly as directed in the last method (page 143). If the combustion is to be made in a current of oxygen, which is much the best plan, instead of drawing the combustion-tube out to a point and sealing it, it may be drawn out straight, as shown in Fig. 65. In this case, attach to the drawn-out end when the tube is in the furnace a purifying apparatus for oxygen and air, as shown in Fig. 56, and conduct the operation as directed on page 143.

FIG. 65.



B. 1. Volatilization of the Iron in a Current of Chlorine, and Subsequent Combustion of the Carbon.

Spread out evenly 1 gramme of pig-iron or 3 grammes of steel on the bottom of a porcelain boat about 3 inches (75 mm.) long, and treat it exactly as described on page 71. The boat when withdrawn from the tube contains the carbon, slag, and oxides, and nearly all of the non-volatile chlorides, such as manganous chloride. When the sample contains much manganese, it is necessary to treat the residue in the boat with cold water, filter it on a small plug of ignited asbestos, return it to the boat, and dry it before burning it off. As this adds very considerably to the time required for the determination, it is best to adopt some other method for the determination of carbon in such materials as spiegel and ferro-manganese. Introduce the boat into the tube B of the apparatus Fig. 66, through which runs the porcelain tube B. This tube is about 25 inches (625 mm.) long and ¾ inch (18 mm.) internal diameter. It projects 6 inches (150 mm.) outside the furnace at each end, and the sheet-iron screens L prevent the heat from reaching the stoppers P and S. The tube is filled for a length of 6 inches (150 mm.), or from about the middle of the tube to the forward end of the furnace, with cupric oxide, which is best made by rolling up tightly a piece of coarse copper gauze 6 inches (150 mm.) long until it makes a roll *nearly* filling the bore of the tube, and heating it for an hour in a current of oxygen. A piece of thin sheet-silver 4 inches long, and forming a roll completely filling the bore of the tube, is placed just in front of the copper dioxide; it serves to absorb any chlorine given off during the combustion.* A roll of copper gauze two inches long, with a loop in one end, thoroughly oxidized, is pushed in after the boat containing the carbon. The cylinder O contains oxygen under pressure. The bottles F, F serve to force air through the apparatus to replace the oxygen at the end of the operation. The stopcock T serves to regulate the flow of water, and consequently of air. When all the water has run

* This roll of silver must occasionally be removed and ignited in a current of hydrogen to remove the chlorine.

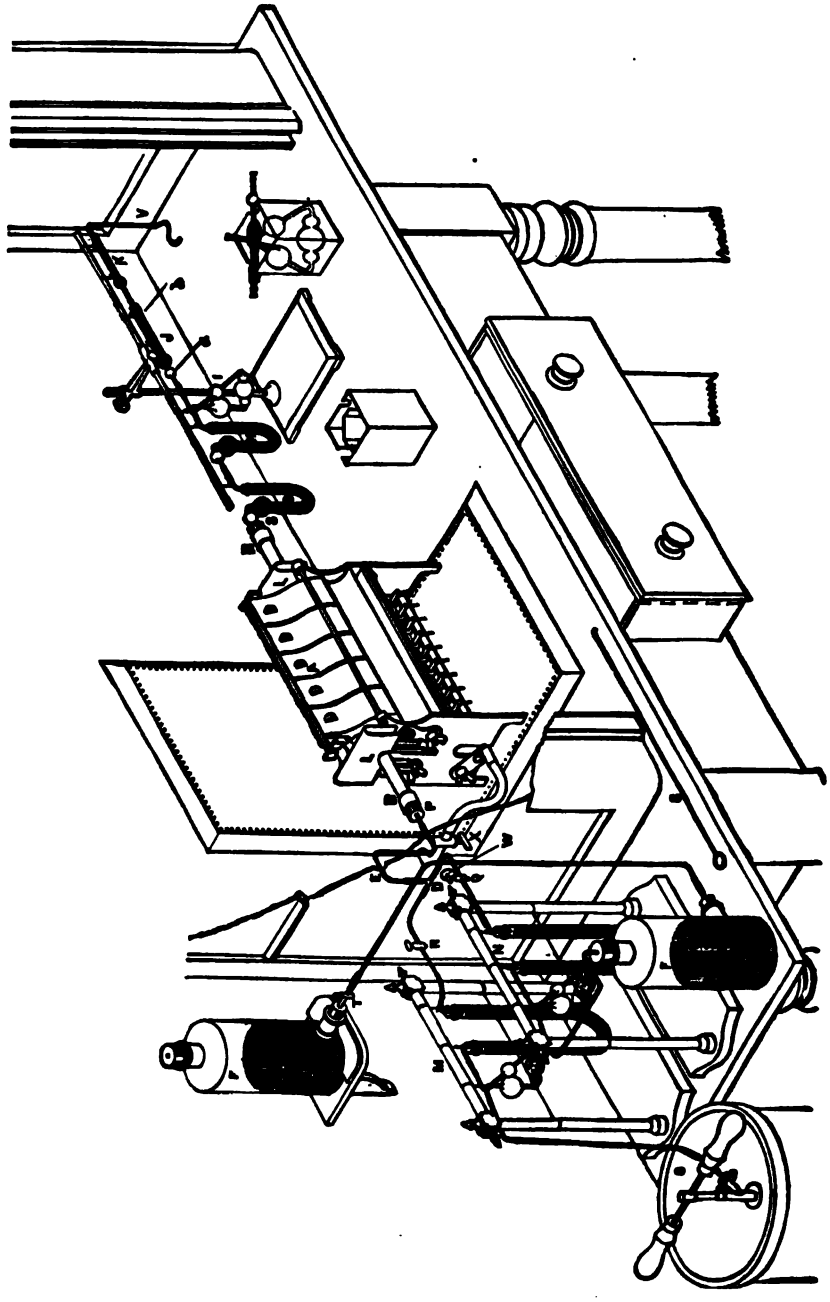


FIG. 66.

from the upper into the lower bottle, it is siphoned out of the latter and returned to the former.

The purifying apparatus M and N, for oxygen and air respectively, consist of Liebig potash-bulbs filled with solution of potassium hydrate (1.27 sp. gr.), and U-tubes, the sides next the potash-bulbs filled with dry pumice and the other sides with calcium chloride. The glass stopcocks Q and R shut off the purifying apparatus on their respective sides when the oxygen or air is passing through the other set. The T-tube D connects the two sets of apparatus, the third limb passing through the glass in the side of the hood, and connecting by means of the bent glass tubes with the rubber stopper P, which fits in the porcelain tube B. All the connections are made with glass tubes joined together by rubber tubing, the ends of the glass tubing being brought close together inside the rubber. This is to avoid carrying the oxygen or air through rubber tubing, which gives off volatile hydrocarbons. The Marchand U-tube G contains anhydrous cupric sulphate to absorb any hydrochloric acid which may be evolved during the combustion. It is joined to the tube B by a rubber stopper. The U-tube H contains granulated dried calcium chloride.* The absorption apparatus is that described on page 132.

The form of absorption apparatus here figured is only one of many that may be used for this purpose. It has the advantage of simplicity and it can be easily wiped clean from any moisture that it may get by handling, from dust, or from gases of the laboratory. The arrangement shown in I, Fig. 78, page 160, is also very convenient. It stands on the pan of the balance, and, when once put together and wiped clean, it may be managed so that the hands come in contact with it as little as possible. On the other hand, the potash-bulb is rather difficult to fill, and the drying tube is necessarily smaller and contains less calcium chloride, so that a very rapid current of air or oxygen may carry moisture from the potash-bulb through it on account of the smaller surface of the drying material. Instead of a potash-bulb a U-tube containing soda-lime is sometimes used, but as soda-lime absorbs carbonic acid only on the surface of the particles, it is not so certain in its action and is not to be recommended. No matter what form of apparatus is selected, care must

* See page 48.

be used to fill the potash-bulb frequently with fresh potassium hydrate and the drying tube with dry calcium chloride.

300 grammes of potassium hydroxide to the litre of water give a solution of 1.27 sp. gr.

Place the absorption apparatus on the balance and allow it to remain about thirty minutes to get the exact temperature, and weigh. Attach the absorption apparatus as shown in the sketch, Fig. 66, insert the boat in the tube by means of the rod C, pushing it up against the cupric oxide, insert the short roll of oxidized gauze as far as the inside of the screen L, and close the tube with the stopper P. Shut the stopcocks R and Q, and, by applying suction at V, draw a few bubbles through the potash-bulb I. When the liquid recedes in the potash-bulb, it should keep its level for a few minutes; if it does not, there is a leak in some of the connections, which must be discovered and stopped before proceeding with the combustion. When everything is tight, open R and start a slow current of oxygen through the apparatus. Light the two forward burners of the furnace, turning them low to heat the oxidized copper gauze, raise the heat gradually until the tube appears red, and then light the last burner to heat the short roll of oxidized copper gauze. As soon as this end of the tube is hot, light the third burner from the forward end, and a few minutes afterwards the fourth burner, which is directly under the forward end of the boat. Light each burner in succession from this one until all are lighted and turned high enough to heat the tube red hot. Allow them to burn for fifteen minutes, then shut off the oxygen, close R, open Q, and by means of the stopcock T start a current of air through the apparatus. By means of the gascock X lower all the lights of the furnace together very slowly, to avoid cracking the tube, and finally turn them out. About 1 litre of air should run through at the rate of three bubbles a second; this will about half empty the upper bottle L. Close T and Q, detach the absorption apparatus, close the ends of I and J with the little rubber caps, and, after wiping the bulb and tube gently with the linen handkerchief to remove any moisture caused by the handling, place them on the balance. Weigh with the same precautions as before;

the increase in weight is carbonic acid, which contains 27.27 per cent. carbon. When several combustions are to be made in succession, as soon as the absorption apparatus is detached as directed above, remove the boat from the tube, replace it with another containing a second sample, attach a second absorption apparatus which has just been weighed, and proceed with the combustion. While the second combustion is in progress, the first absorption apparatus may be weighed, and the weight then obtained can be used for the first weight of the absorption apparatus for a third combustion. Before the absorption apparatus shall have increased .5 gramme in weight from the original weighing, the potash-bulb must be emptied and refilled with a fresh solution. When the final combustion for the day is finished, place a piece of glass rod in the open end of the connection of H, remove the boat from the tube B, replace the short roll of oxidized copper gauze in the tube, insert the stopper P, but not tightly, open R and Q, and loosen the stopper in the bottle F. Place pieces of glass rod in the ends of the safety-tube K, to prevent access of moisture. Whenever the apparatus has been out of use for a day, before making a combustion or set of combustions remove the piece of glass rod from the forward end of the U-tube H, insert in its place a piece of glass tubing drawn out at the forward end to a small orifice, start a current of oxygen through the apparatus, light the burners in the furnace, raising the heat very gradually, keep the tube at a red heat fifteen minutes, turn off the oxygen, start the air, lower the burners gradually, and pass a litre of air through the apparatus. It will then be ready for the combustion. In very damp weather it is almost impossible to get good results, the condensation of moisture on the absorption apparatus rendering the weighing extremely difficult even when the utmost care is used.

This difficulty may be overcome almost entirely by using another absorption apparatus of similar form as a counterpoise. This counterpoise should be arranged to weigh 2 or 3 grammes less than the absorption apparatus. The superficial area of the two being practically equal, the condensation on the two surfaces is the same.

The calcium chloride in the drying-tube of the absorption apparatus must frequently be renewed, as it absorbs the moisture carried over from the caustic potash, and the success of the operation depends upon the *oxygen and air leaving the absorption apparatus in the same hygroscopic condition as when they enter it.*

2. Volatilization of the Iron in a Current of Hydrochloric Acid Gas, and Subsequent Combustion of the Carbon.

The process is exactly the same in this method as in that just described, a current of hydrochloric acid gas being substituted for one of chlorine. The apparatus for generating this gas is the same as the one used for chlorine, common rock-salt in pieces about as large as a filbert being substituted for manganese dioxide, and sulphuric acid, diluted with two-thirds its bulk of water, for hydrochloric acid.

C. 1. Solution in Potassium-Cupric Chloride, Filtration, and Weighing or Combustion of the Residue.

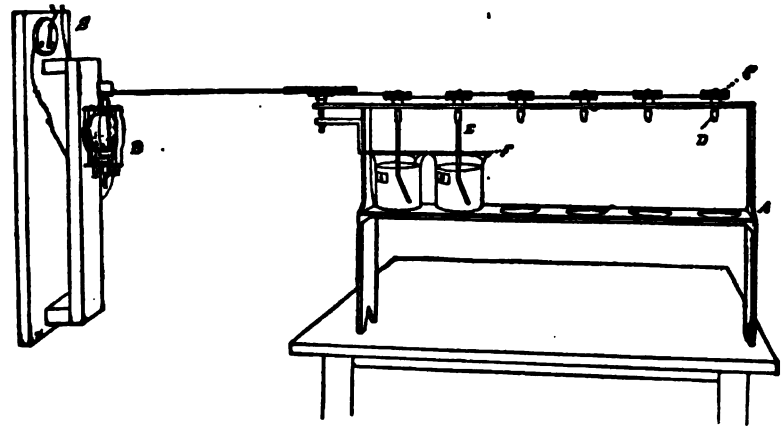
Place 1 gramme of pig-iron, spiegel, or ferro-manganese in a 400 c.c. beaker, and add 100 c.c. of a saturated solution of potassium-cupric chloride and 7.5 c.c. hydrochloric acid. For steel or puddled iron, use 3 grammes and add 200 c.c. of potassium-cupric chloride solution and 15 c.c. strong hydrochloric acid. Stir the solution constantly with a glass rod for some minutes at the ordinary temperature. The more it is stirred the more rapid will be the solution of the iron and of the precipitated copper. The beaker, carefully covered, may now be placed on the top of the air-bath or on a cool part of the iron plate, but the solution should never be heated hotter than 60° or 70° C., and it should be stirred as often as practicable.

As the most tedious part of the determination of carbon in steel is frequently that which has to do with the decomposition of the steel and the solution of the precipitated copper, particularly in the case of low steels, the samples being nearly always in lumps, and it not being desirable to separate these larger particles for fear that the fine stuff alone may not represent a true average, the machine shown in Fig. 67 is very useful.

It consists of a framework, A, of brass, cast in one piece for the sake of rigidity. It is fastened to the table by lugs and screws not shown in the cut. The shelf on which the beakers stand has on it a piece of asbestos board with holes to fit exactly the bottoms of the beakers to prevent them moving. To further increase the stability of the beakers (which should be of very heavy glass) their bottoms are ground on a glass plate with fine emery until they have a good bearing surface all around.

The tops, which are covered when on the machine with a plate of glass, F, ground on one side and perforated to allow the passage of the stirring-rods, E, are likewise ground, so that when slightly moistened the ground glass prevents almost entirely all movement of the covers on the beakers when the machine is in motion.

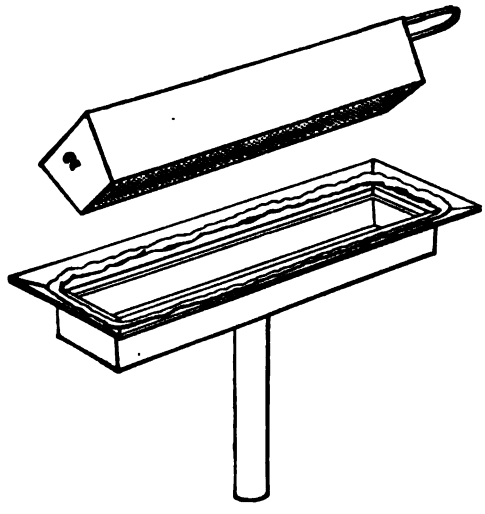
FIG. 67.



The small wooden pulleys are fitted with brass spindles, which run through the upper cross-piece and have on their lower ends pieces of rubber tubing, which serve to hold the stirring-rods. The stirring-rods are bent as shown in the cut, to give the proper motion to the liquid. A small motor, B, adapted to the strength of the current, furnishes the requisite power. The motor, if properly wound, may be attached to an ordinary incandescent lighting current, but a sewing-machine motor run by a dipping battery of three bichromate cells is sufficient to give the necessary number of revolutions.

The fact that it is not only unnecessary to use a neutral solution, but that the use of a neutral solution gives inaccurate results, seems now to be thoroughly established by the experiments of the American members of the International Steel Standards Committee. The best practice is to add about 10 per cent. of hydrochloric acid to the solution of the potassium-cupric chloride. The reactions occurring may be considered as $Fe + CuCl_2 = FeCl_2 + Cu$ and $Cu + CuCl_2 = 2CuCl$. The part taken by the potassium chloride does not seem very clear, but the fact remains that the precipitated copper is much more soluble in the double salt than in any other menstruum. When the precipitated copper is all, or very nearly all, dissolved, which is usually the case in half an hour after the solution of potassium-cupric chloride is added to the drillings, run a little of the acidulated double chloride around the beaker with a jet of water, and let the beaker stand for a few minutes to allow the carbonaceous matter to settle.* The best form of filtering-apparatus is shown in the annexed sketches. It consists of the perforated platinum boat (Fig. 68), which fits in the platinum holder. To prepare the boat for use, place it in the holder, as shown in Fig. 69, attach the pump, but do not start it. Fill the boat with prepared asbestos † suspended in water, pour enough around the outside of the boat to fill the space *a*, Fig. 69, and start the filter-pump. Continue pouring the suspended asbestos into the space *a*, Fig. 69, until enough is drawn into the joint to make a good packing. By pressing it in all

FIG. 68.

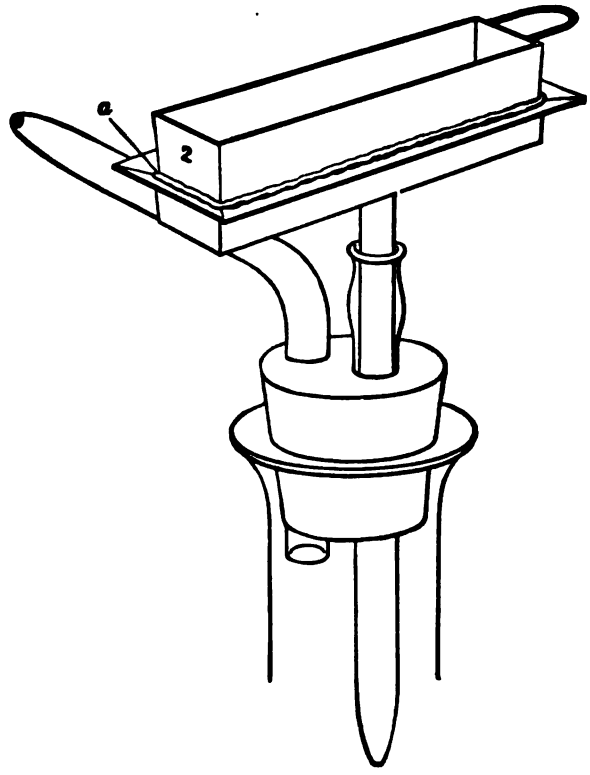


* Barba suggests adding to the solution ignited asbestos in water to make the carbonaceous matter settle and to prevent its clogging the filter. This is a most admirable suggestion and should be generally adopted.

† See page 23.

around with a spatula the joint may be made very tight. Pour enough of the suspended asbestos into the boat to make a good, thick felt, and press it down firmly all over the bottom of the boat with something like the end of a lead-pencil, to make it compact. Detach the pump, remove the boat from the holder carefully so as to leave the packing on the sides of the holder, and move it up with the end of a spatula,

FIG. 69.



so that it will remain as shown in Fig. 68. Place another boat in the holder, press the packing into the joint *a*, Fig. 69, with the end of a spatula, fill the boat with suspended asbestos, and start the pump. If necessary, pour a little of the finer suspended asbestos fibre into the joint to make it perfectly tight, and prepare the felt in the boat as before. Dry the boats, and ignite them in the combustion-tube, two at a time,

in a current of oxygen. Fit one of these prepared boats in the holder, press the packing into the joint as before, first moistening it slightly if it has become dry, start the pump, and pour into the boat enough suspended asbestos, which has been ignited in oxygen, to form a thin film on the top of the felt. This film will hold the silica, ferric phosphate, etc., from the carbonaceous residue, and, after the combustion, will usually turn up at the edges, so that it can readily be detached from the main felt, leaving the boat ready for another filtration.

The boat being thus prepared, pour into it the solution of the iron or steel, guiding the stream by a small glass rod held against the tip of the beaker. The solution, if the joint *a*, Fig. 69, is tight, and the pump works well, will usually run through the felt as rapidly as it can be poured into the boat. When the supernatant fluid has all run through, transfer the carbonaceous matter to the boat by a fine stream of cold water from a washing-flask. Pour into the beaker about 10 c.c. of dilute hydrochloric acid, run it all around the inside of the beaker by means of the rod to dissolve any adhering salt, wash the glass rod and wash down the sides of the beaker with a jet of water, and decant the acid into the boat, filling it almost up to the edge. Wash the carbonaceous matter in the boat thoroughly with hot water by filling the boat from the beaker and allowing it to suck through dry, but do not attempt to throw a jet of water into the boat from the washing-flask, as it will be almost certain to throw some of the carbonaceous matter from the boat or cause it to crawl over the side. In decanting the water from the beaker, the lip must not be allowed to touch the surface of the liquid in the boat, as a film of carbonaceous matter will run up the inside of the beaker. Pour a little dilute acid into the joint between the boat and holder, allow it to suck through the packing, and wash it several times with hot water. The carbonaceous matter from pig-iron, puddled iron, spiegel, ferro-manganese, and ingot steel usually washes like sand, but that from steel which has been hardened, tempered, hammered, or rolled is apt to be more or less gummy, stopping the filter and rendering the filtration and washing prolonged and tedious. It is also apt to adhere more or less to the sides of the beaker, and must

be wiped off by a little wad of ignited fibrous asbestos, held in a pair of platinum-pointed forceps like those shown in Fig. 70.

This wad is then placed in the boat. When the carbonaceous matter is thoroughly washed and sucked dry, detach the pump, remove the boat from the holder, wipe the outside carefully with a piece of silk, place it in a dish covered with a watch-glass, and dry it in a water-bath or an air-bath at 100° C. When dry, insert the boat in the tube (Fig. 66), and burn off the carbon as directed on page 148. Instead of the porcelain tube, a platinum tube, of the dimensions shown in Fig. 54, page 130, may be used to very great advantage. The U-tube C contains water. The limb of the U-tube D nearest the platinum tube contains anhydrous cupric sulphate * and the forward limb anhydrous cuprous chloride.† E contains dried, *not fused*, calcium chloride, and in the bulb next to G is a small wad of cotton-wool. The object of the cuprous chloride is to absorb any chlorine that may cover over during the combustion. If any should come over it would be mixed with hydrochloric acid and moisture, and all then would be absorbed by the water in C and the salts in the tube D. The burners in the furnace should be lighted in the order directed on page 148, and, after they are all lighted, ten minutes' time is ample to burn off the carbonaceous matter in the boat. From the time of putting in the boat, fifty minutes' time is ample for finishing the combustion, including the displacement of the oxygen by air.

FIG. 70.

The time required when using a porcelain tube is somewhat longer, owing to the danger incurred of cracking the tube if the heat is increased or diminished too rapidly. A platinum tube shorter than the one here figured is not to be recommended, as it cannot contain enough oxygen to burn the carbon to carbonic acid, and a consequent loss is often unavoidable. Duplicate results by this method should rarely vary more than .005 of a per cent. carbon. When using 3 grammes of the sample, the percentage of carbon is obtained by dividing the weight of carbonic acid by 11 and multiplying by 100.

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* See page 49. † See page 49.

Instead of the perforated boat and holder described above, the carbonaceous residue may be filtered in a small platinum tube fitting inside the combustion-tube. It is made as represented in Fig. 71.

FIG. 71.

The small perforated disk of platinum rests on a seat in the tube as shown in the sketch. The felt on the disk is prepared in the same way as directed for the boat, and, after drying the carbonaceous residue, the disk is moved upward in the filtering-tube, to allow the gas to pass through the filtering-tube during the combustion. The boat has several advantages over the filtering-tube, the principal one being that the boat has a much larger filtering-surface, and, besides, there is no danger of the felt being disturbed during the filtering, while the disk in the tube may be loosened in its seat and allow some of the carbonaceous matter to pass around it. If the boats when not in use are kept carefully covered, the same felts may be used for a large number of filtrations; but occasionally they become clogged, and then it is better to renew them.

FIG. 72.

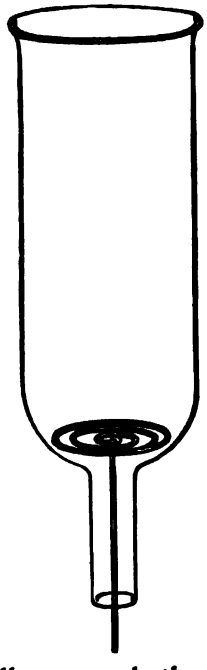
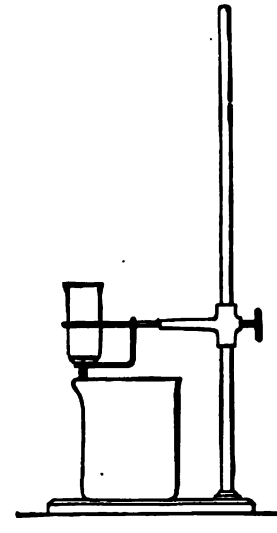
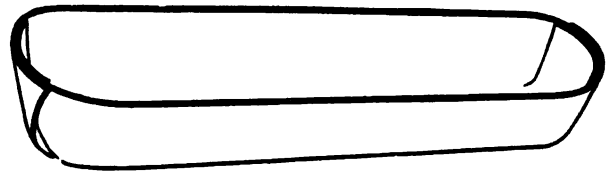


FIG. 73.



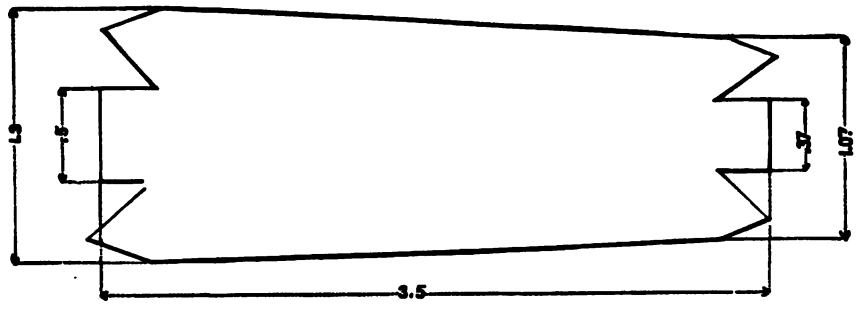
Instead of either of these forms of filtering-apparatus, a simple glass tube, as represented in Fig. 72, may be used. The closely coiled spiral of platinum wire fits in the tube as shown in the sketch. On this is placed a rather thick layer of ignited long-fibre asbestos, and ignited asbestos suspended in water is poured over it to make a

FIG. 74.



solid felt. The tube may be used in a stand, as represented in Fig. 73, or it may be used with the filter-pump under very gentle pressure. Filter and wash the carbonaceous matter, and while still moist transfer it to the boat (Fig. 74) by opening out the sides of the boat, inverting the tube over it, and allowing the felt and spiral to slide out of the tube. Wipe off any carbonaceous matter that may remain on the

FIG. 75.



sides of the tube, or that may have adhered to the spiral in removing it, with little wads of fibrous asbestos held in the forceps (Fig. 70). Place these wads in the boat, bend the sides of the latter into their proper shape, dry the boat and contents at 100° C., insert the boat in the porcelain or platinum tube, and burn off the carbonaceous matter as before directed. This boat is made by cutting a piece of platinum-

foil in the shape shown in Fig. 75, and bending it up over a brass former into the shape shown in Fig. 74.

Instead of burning the carbonaceous matter in a current of oxygen, it may be burned by sulphuric and chromic acid in the arrangement shown in Fig. 76. P′ is an empty U-tube, O is a tube containing silver sulphate dissolved in strong sulphuric acid, P contains anhydrous cupric sulphate, Q granular dried calcium chloride, a Liebig bulb and drying-tube R constitute the absorption apparatus, S is the safety-guard tube, and L, L constitute the arrangement for passing air through the apparatus. The air is freed from carbonic acid in passing through the U-tube M filled with lumps of fused potassium hydroxide. Transfer the carbonaceous matter and asbestos to the flask A, insert the stopper carrying the bulb-tube B, close the stopcock C, and connect the apparatus as shown in Fig. 76, including the weighed absorption apparatus. See that the joints are all tight, and then pour into B 10 c.c. of a saturated solution of chromic acid, admit it to the flask A by opening the stopcock C, and then pour into B 100 c.c. strong sulphuric acid with a little chromic acid which has been heated almost to boiling. Let this run into A slowly, connect the air apparatus by the tube N, and start a slow current of air through. Light a very low light under A, and increase it gradually until the liquid is heated to the boiling-point. Gradually lower the light while the current of air continues to pass, and when about 1 litre of air has passed through the apparatus after the light is extinguished, detach and weigh the absorption apparatus, with the precautions mentioned on page 133.

The carbonaceous residue may also be weighed directly instead of being burned off. In this method, filter on a Gooch crucible or on counterpoised filters,* dry at 100° C., and weigh. Burn off the carbonaceous matter and weigh the residue: the difference between the two weights is carbonaceous matter, which contains about 70 per cent. of carbon † in steel or iron free from graphite. Of course this method of direct weighing is applicable only to samples when all the carbon is in the so-called combined condition.

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* See page 29.

† American Chem. Jour., iii, 245.

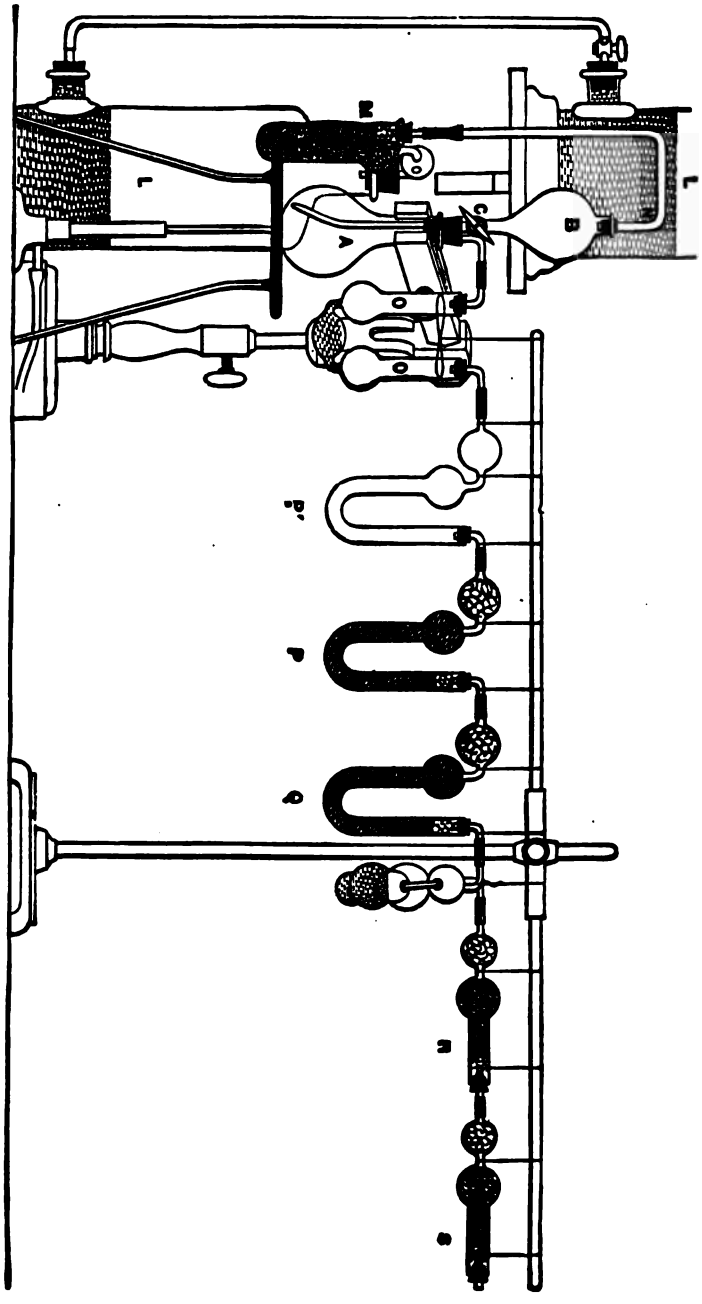
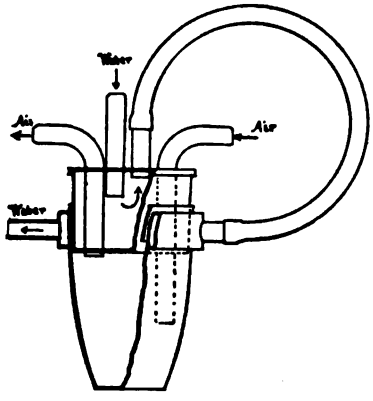


Fig. 76.

Combustion in the Shimer Crucible.

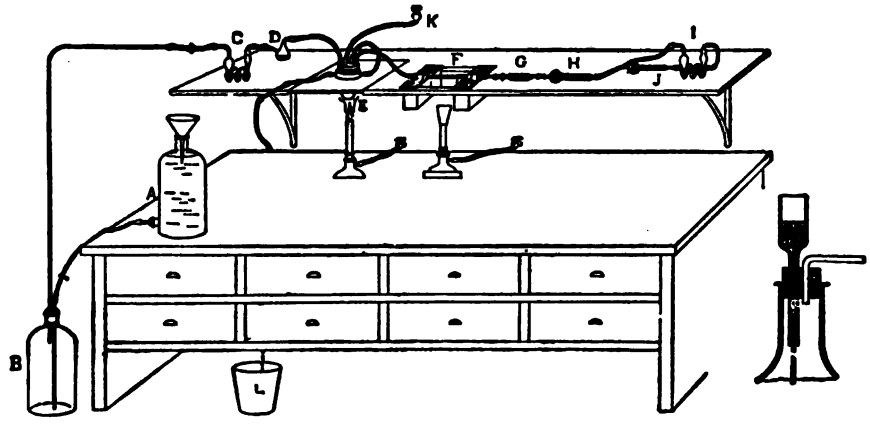
In this apparatus combustion is effected in a special water-jacketed platinum crucible (the details of which are shown in Fig. 77) closed by a hollow water-cooled stopper made of brass. An ordinary rubber band around the stopper insures a tight joint, and the water passing through it and around the upper part of the crucible prevents the rubber from softening when the lower half of the crucible is heated to a high temperature. For combustion of carbon from steel or pig-iron air alone is used. Other novel parts of the apparatus are a small brass tube for cupric oxide; a glass tube filled with glass beads, wet with water, for retaining hydrochloric acid and chlorine; and a special funnel for rapid filtration and transference of the carbon.

FIG. 77.



Beginning at the left, Fig. 78, the train of apparatus, conveniently disposed on a heavy asbestos board shelf, is as follows:

FIG. 78.



For air-pressure, a large aspirator bottle, A, filled with distilled water, and connected with a lower bottle, B, by means of a tube reaching to the bottom of the latter. C, potassium hydroxide bulbs. D, a small guard

bottle. The crucible, E, connected with a water supply, K, and waste, L. The crucible is supported by passing it about half-way through a heavy piece of asbestos board. Under the crucible an adjustable Bunsen burner or an upright blast-lamp. A brass tube, F, containing rather fine cupric oxide, but free from powder, in its central portion, is heated to a red heat by a special burner, for about two inches. This tube is twelve inches long and is $\frac{7}{16}$ inch in external diameter. Attachments are made by passing the rubber tubing over the heads of the tube which is supported in a rectangular opening in the shelf. The ends of the tube are cooled by a long piece of heavy blotting-paper fastened around each end and dipping into the water contained in tin boxes attached to the shelf. The glass-bead tube, G, internally wet with distilled water and externally cooled by wet filter-paper, for retaining hydrochloric acid and chlorine. A large calcium chloride tube, H. Potassium hydroxide bulbs and drying tube, I. A guard-tube of calcium chloride, J.

The carbon is filtered on a filter-tube ⅞ inch in internal diameter. A small glass rod, flattened out at the end, passes through the stem of the funnel and projects several inches beyond. A mass of glass wool ½ inch deep is packed into the bottom of the tube, and on this is deposited, under suction, the filter, about ⅛ inch deep, of finely divided ignited asbestos. After filtration and washing the contents of the tube are pushed up by means of the projecting glass rod until the filter projects. The filter can now be easily picked off the glass wool base by use of a curved forceps. The carbon may be quickly and conveniently dried by placing the filter upon a previously warmed and labelled scorifier.

In direct combustions of difficultly soluble alloys mix 0.2 gramme of the finely pulverized sample with 2.5 grammes of pulverized lead chromate, place the mixture in a porcelain crucible, cover with 0.5 gramme of the chromate, and heat for an hour in a current of oxygen.

2. Solution of the Iron in Cupric Sulphate, Filtration, and Combustion of the Residue in a Boat in a Current of Oxygen.

To 3 grammes of steel in a 400 c.c. beaker add 150 c.c. of solution of cupric sulphate, made by dissolving 200 grammes of the copper salt in water, adding a dilute solution of caustic soda until a slight

permanent precipitate appears, allowing it to settle, filtering through asbestos, and diluting to 1 litre. For pig-iron, spiegel, and ferro-manganese, use 1 gramme, and 50 c.c. of cupric sulphate solution. Heat the solution gently, and stir well until decomposition is complete. Filter in a glass filtering-tube on asbestos, as described on page 157. Wash well with water, transfer to a boat, as directed on page 157, dry, and burn in a porcelain tube, as directed on page 148. The results are apt to be a little low, owing to the difficulty of thoroughly oxidizing the mass of copper mixed with the carbonaceous matter.

Instead of filtering off the mass of copper, carbonaceous matter, etc., decant the clear supernatant fluid through the filtering-tube, wash several times by decantation, and then dissolve the copper in potassium-cupric chloride, cupric chloride, or ferric chloride. Filter, wash the residue with a little dilute hydrochloric acid, and then with cold water, transfer to a boat, and burn as directed on page 148.

3. Solution of the Iron in Cupric Sulphate, and Oxidation of the Residue by Chromic and Sulphuric Acids.

Treat the sample with solution of cupric sulphate, as in the method just described. Allow the precipitated copper and carbonaceous matter to settle, pour off the clear supernatant liquid, and transfer the residue to the flask A (Fig. 76, page 159) by means of a platinum spatula and a fine jet of water. The water used should not exceed 20 or 25 c.c.* The apparatus is that sketched in Fig. 76, the only difference being that the tube O contains merely a little strong sulphuric acid. Effect the combustion exactly as described on page 158.

DETERMINATION OF GRAPHITIC CARBON.

Karsten gave the first information in regard to the existence of graphite in pig-iron, and he suggested dissolving the sample in nitric acid with the addition of a few drops of hydrochloric acid, in hydrochloric acid alone, or in dilute sulphuric acid, boiling the residue with caustic potash, filtering, washing again with hydrochloric acid and finally with water, and

* Trans. Inst. Min. Engineers, iii, 42.

weighing the residue as graphite. A very interesting comparison of the results obtained by the use of different solvents is given by Drown.* The usual method is as follows: Treat 1 gramme of pig-iron or 10 grammes of steel with an excess of hydrochloric acid (1.1 sp. gr.). When all the iron is dissolved, boil for a few minutes, allow the graphite to settle, and decant the supernatant fluid on an asbestos filter, using either the perforated boat, Fig. 68, or the filtering-tube, Figs. 71 and 72. Wash several times with hot water by decantation, then pour on the residue in the beaker 30 c.c. of a solution of caustic potash (sp. gr. 1.1), and, when the effervescence ceases, heat the solution to boiling. Filter on the same filter, transfer the graphite, etc., to the filter, wash with hot water again, and finally with alcohol and ether. Burn the graphite by one of the methods given under "Determination of Total Carbon," and from the weight of carbonic acid obtained calculate the percentage of carbon existing as *graphite.* It frequently happens, when the sample is a high steel, that the residue which remains after treating it as above is black, and contains carbon, but it is not crystalline in appearance, and bears no resemblance to graphite. The same steel will dissolve completely in nitric acid, and when filtered will not leave a trace of carbon on the felt. Steels containing graphite give appreciably less carbon when dissolved in nitric acid than when dissolved in hydrochloric acid. The method giving probably the most accurate and certainly the most uniform results is as follows: Dissolve the weighed sample in nitric acid (sp. gr. 1.2), using 15 c.c. of acid to each gramme taken for analysis. Filter on the perforated boat or on an ignited asbestos filter, in a glass tube, transfer the residue to the filter, and wash thoroughly with hot water. Treat the residue on the filter with hot caustic potash solution, 1.1 sp. gr. (as the silicon is all oxidized to silica there will be no effervescence), wash thoroughly with hot water, then with a little dilute hydrochloric acid, and finally with hot water. Burn the carbon by one of the methods previously mentioned and calculate the carbonic acid obtained to carbon, and call the result *graphite.*†

* Trans. Inst. Min. Engineers, iii. 42.

† Shimer (Jour. Amer. Chem. Soc., xvii. 873) has shown that titanium carbide is insoluble in dilute hydrochloric acid and that the nitric acid method is the only accurate one for the determination of graphite.

DETERMINATION OF COMBINED CARBON.

Indirect Method.

Having determined the total carbon and the graphite, by subtracting the latter from the former we obtain the amount of carbon existing in the *combined condition.*

Direct Method.

This method was first introduced by Eggertz* in 1862. It is based on the fact that when steel containing carbon is dissolved in nitric acid (1.2 sp. gr.), the carbon, which sometimes at first separates out in flocks of a brownish color, is eventually dissolved, giving to the solution a depth of color directly proportionate to the amount of combined carbon in the steel. To use this in practice it is only necessary to determine accurately the amount of combined carbon contained in a steel, by a combustion method, and to compare the depth of color in a solution of this standard with that of any unknown steel, in order to ascertain the amount of carbon in the latter. There is, however, a limitation to the application of this method. Reference was made on page 126 to the fact that combined carbon is now believed to exist in two conditions in steel, or rather that under certain circumstances a portion of the combined carbon changes its condition, and, from a chemical point of view, while it is still combined carbon, in that it is soluble in nitric acid, it fails to impart so dark a color to its nitric acid solution as it did in its original state. The circumstances under which a change of this kind occurs are quite well known, and are merely those occasioned by the mechanical treatment to which steel is submitted, such as hammering, rolling, hardening, tempering, etc.† It may be stated, then, as a general proposition, that *the standard steel for the color-test should be of the same kind and in the same physical condition as the samples to be tested.*

To obtain the best results samples should be taken from the original ingots which have not been reheated, rolled, or hammered; Bessemer

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* Jern-Kontorets Annaler, 1862, p. 54; 1874, p. 176; 1881, p. 301; Chem. News, vii. 254; xliv. 173.

† Two very interesting papers on this subject will be found in the Chem News, J. S. Parker, "On the Varying Condition of Carbon in Steel," xlii. 88; T. W. Hogg, "On the Condition of Carbon in Steel," xlii. 130.

steel should be compared with Bessemer, crucible with crucible, open hearth with open hearth; the standard should contain approximately the same amount of carbon as the samples to be tested, and should have as nearly as possible the same chemical composition. The only elements that seem to have any decided effect on the color of the nitric acid solution are copper, cobalt, and chromium.

Weigh out carefully .2 gramme of each sample, including the standard, into test-tubes 6 inches (150 mm.) long and ⅝ inch (16 mm.) in diameter. The test-tubes should be perfectly clean and dry, and each one marked with the number of the sample on a small gummed label near the top. A little wooden rack (Fig. 79) is convenient for holding the test-tubes in the weighing-room, and to avoid all chance of error the tube is not placed in the rack until the sample has been weighed and is ready to be transferred. A little platinum or aluminum dish about 1½ inches (40 mm.) in diameter, with a spout, and furnished with a counterpoise (Fig. 42, page 33), is very convenient for holding the drillings, which are brushed from it into the test-tube with a

FIG. 79.

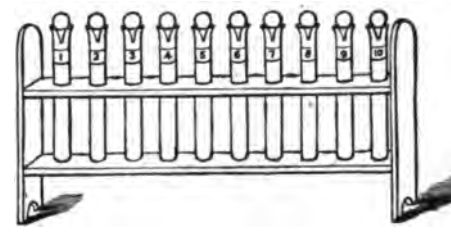
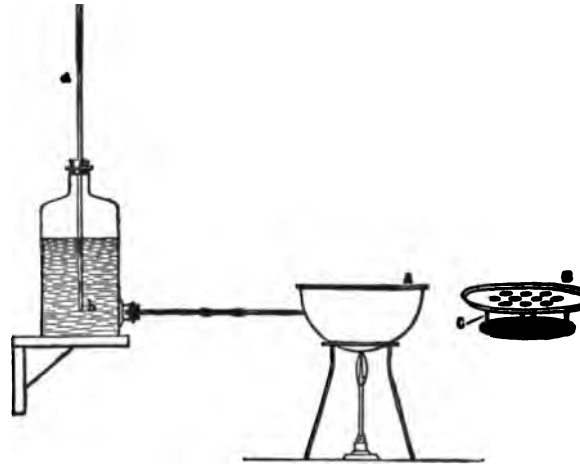


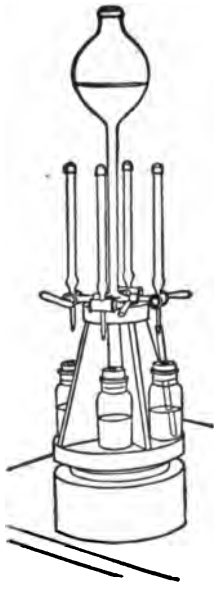
FIG. 80.



camel's-hair brush. A very excellent form of water-bath is shown in Fig. 80. It may be provided with a constant level arrangement, consisting of a tabulated bottle, the height of the end *b* of the vertical tube *a* fixing the level of the water in the bath. A is the bath and B the rack. The top of the rack is of sheet-copper, perforated to receive the test-tubes, the bottoms of which rest on the coarse copper gauze, which is joined to the top by the uprights C. The top of the rack rests on a flange around the top of the bath.

Place the test-tubes in the rack B, and stand the rack in the bath which contains cold water. Drop into each test-tube, from a pipette, the proper amount of nitric acid (sp. gr. 1.2). For steels containing less than .3 per cent. carbon use 3 c.c. nitric acid; from .3 to .5 per cent. carbon, 4 c.c.; from .5 to .8 per cent., 5 c.c.; from .8 to 1 per cent., 6 c.c.; and over 1 per cent., 1 c.c. An insufficient amount of acid gives the solution a slightly darker tint than it should properly have.

FIG. 81.



The apparatus shown in Fig. 81 * is useful for the rapid addition of measured quantities of nitric acid to the samples.

It consists of a glass reservoir holding 750 c.c., communicating below with four burettes graduated to *deliver* various quantities of acid up to 10 c.c. Each burette is furnished with a loose-fitting glass cap. The burettes are fitted with three-way glass stopcocks, so that a quarter of a revolution connects them with the reservoir, and when the proper amount of acid has run in, the stopcock is turned another quarter, which shuts off the reservoir and completely empties the burette, thus delivering the exact amount of acid measured into the test-tube containing the weighed sample of steel in which carbon is to be determined.

As shown in the cut, each test-tube stands in a bottle of cold water to prevent too violent action of the acid during solution. The whole

* Communicated to the author.

apparatus is mounted on a rotary stand, and, as used at the laboratory of the Bethlehem Iron Company, is contained in a small hood near the drill and balance described on page 13, so that the operator, seated on a revolving stool, can add acid to one sample of steel while the drillings of the next are falling into the balance-pan.

The apparatus, as here shown, is a modification by Mr. Albert L. Colby, of the Bethlehem Iron Company, of an apparatus first designed by Mr. E. A. Uehling in 1884.

The nitric acid is made by adding its own volume of water to acid of the usual strength (1.4 sp. gr.). It should be absolutely free from chlorine or hydrochloric acid, as, according to Eggertz, .0001 gramme chlorine in a nitric acid solution of .1 gramme iron in 2.5 c.c. nitric acid gives a decidedly yellow color. The nitric acid should be added slowly, to prevent violent action, and the drillings should not be too fine, for the same reason. Place in the top of each test-tube a small glass bulb * or a very small funnel, heat the water in the bath to boiling, and boil until all the carbonaceous matter is dissolved, shaking the tubes from time to time to prevent the formation of a film of oxide. The time required for solution is for low steels about twenty minutes and for high steels (over 1 per cent. carbon) forty-five minutes. After entire solution of the carbonaceous matter, prolonged heating tends to make the color lighter; therefore, as soon as the absence of small bubbles and the disappearance of any brownish flocculent matter show complete solution, remove the rack from the bath and stand it in a dish of cold water. The dish should be about the same size as the bath, so that the top will be covered by the top of the rack, thus excluding the light from the solutions, in which case the color will not fade for a long time. Under all circumstances the solutions should be kept out of the light, and especially out of direct sunlight, as much as possible. If there should be necessarily, in the steels operated on at one time, a wide range in carbon, the test-tubes should be removed from the bath as fast as their respective contents are dissolved and placed in cold water in a

* These bulbs are easily made by sealing one end of a glass tube in the blowpipe flame, heating it, blowing a bulb of the proper size, allowing it to cool, heating it above the neck, and drawing it out as shown in Fig. 79.

dark place. The appearance of the drillings will often give an idea of the approximate carbon contents of a sample, but, when there is no clue whatever, it is best to begin by adding 3 c.c. nitric acid to the weighed portion in the test-tube, and increase the amount 1 c.c. at a time as the depth of color of the solution or the amount of flocculent carbonaceous matter indicates a higher carbon percentage. To compare the colors of the solutions, pour the standard into one of the carbon tubes (Fig. 82), wash out the test-tube with a little cold water, add it to the solution in the carbon tube, and dilute to a convenient amount.

FIG. 82.

This dilution should be sufficient to make the volume of the diluted standard at least twice as great as the volume of acid originally used to dissolve the sample, as this amount of water is necessary to destroy the color due to the ferric nitrate. It should not, however, greatly exceed this amount, and should be some convenient multiple of the carbon contents of the standard in tenths of a per cent. Thus, if a standard contains .45 per cent. carbon, dilute the solution in the carbon tube to 9 c.c., then each c.c. will equal .05 per cent. The carbon tubes should be ½ inch (12 mm.) in diameter, holding at least 30 c.c., and graduated to $\frac{1}{10}$ c.c. The tubes should have exactly the same diameter, and the glass should be perfectly colorless and have walls of the same thickness. They should, of course, be most accurately graduated.

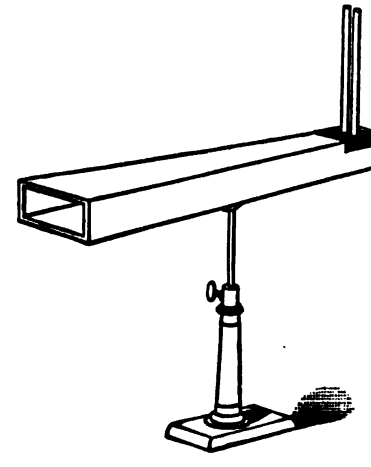
Mr. E. F. Wood,* of the Homestead Works, leaves the lower ends of the tubes free from graduations to give a clear space for comparing the colors. He considers this especially necessary in low steels, for which he uses 1 gramme of the sample, dissolves in 25 c.c. of nitric acid, boils for from five to seven minutes in a glycerine bath at 140° C., and compares in tubes ¾ inch (18 mm.) in diameter.

The standard having been prepared, pour the solution of the sample to be tested into another carbon tube, rinse the test-tube into it with a little cold water, and compare the colors. If the solution of the sample is darker than that of the standard, add water little by little, shaking the

* Communicated to the author.

tube well to mix the solution until the shades are exactly the same. Allow a minute or two for the solution to run down the walls of the tube, and read the volume. If the standard was diluted as above, then, of course, each c.c. will equal .05 per cent. carbon, and if the volume of the sample is 10.5 c.c. it will contain .525 per cent. carbon. If the solution of the sample when first transferred to the tube should be lighter in color than the standard, a lower standard must be used, or this one may be diluted to, say, 13.5 c.c., in which case the number of c.c. divided by 3 will give the percentage of carbon in tenths. The color may be compared by holding the two tubes in front of a piece of white paper held towards the light, but a camera made of light wood and blackened inside is most convenient, and at night is quite invaluable. It is shown in Fig. 83, and consists of a box 3½ inches (90 mm.) high inside, 1½ inches (38 mm.) wide at one end, and 5 inches (127 mm.) at the other. It is 24 inches (610 mm.) long, and is supported on a rod, which can be raised and lowered to suit the convenience of the observer. The small end is closed by a piece of ground glass, which slides in through a slot on top 1 inch (25 mm.) from the end. Immediately beyond this is another slot to receive a thin piece of faintly blue glass, which is inserted when the tests are made at night, using an oil-lamp placed on a stand just beyond the camera. In fact, in many steel works, to avoid the differences between the colors as seen by daylight and lamplight, *all* comparisons are made in a dark room using a box or camera and an oil-lamp. Two holes in the top of the camera just inside the ground-glass screen receive the carbon tubes, the ends of which rest on a piece of black cloth on the bottom of the camera inside. Another piece of black cloth fastened across the top of the camera, covering the top of the ground-glass slide, and having holes just large enough to admit the tubes, excludes all light except that at

FIG. 83.



the back of the tubes. A north light is much the best for comparing the colors, and, as to most observers the left-hand tube appears a little the darker, the color will be exactly matched when, the tubes being reversed, the left-hand tube still appears a little the darker of the two.

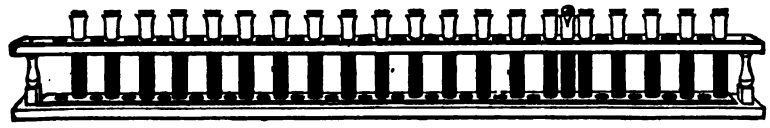
Instead of diluting the solutions to agree with a standard, as above described, some chemists use a rack of permanent standards, as suggested by Britton.* The principal difficulty heretofore attending the use of permanent standards has been the impossibility of preventing their fading; but, according to Eggertz,† this is now entirely overcome by the method of preparing them suggested by Prof. F. L. Ekman. The details are as follows. Dissolve 3 grammes of neutral ferric chloride in 100 c.c. water containing 1.5 c.c. hydrochloric acid; dissolve 2.1 grammes cupric chloride in 100 c.c. water containing .5 c.c. hydrochloric acid, dissolve 2.1 grammes cobaltic chloride in 100 c.c. water containing 5 c.c. hydrochloric acid, using the neutral salts in all cases. These solutions will contain about .01 gramme of the metal to the c.c., and by adding to 8 c.c. of the iron solution 6 c.c. of the cobalt solution, 3 c.c. of the copper solution, and 5 c.c. water containing .5 per cent. hydrochloric acid, a liquid is obtained which has a color approximating that obtained by dissolving .2 gramme of steel, containing 1 per cent. of carbon, in nitric acid, and diluting to 10 c.c., or .1 per cent. carbon to the c.c. Prepare a number of test-tubes of the size described on page 165, but in this case it is essential that they should be of exactly the same diameter, and that the glass should be as nearly colorless as possible. By successive dilutions with water containing .5 per cent. hydrochloric acid, of the normal solution prepared as above, make solutions of about the proper strength for the series required.

The variations should be about .02 per cent. between the different tubes of the series, corresponding to, say, the even hundredths. There should be about 10 c.c. of solution in each tube, and then the color of each should be compared with a standard steel, diluted to the exact strength required in the permanent standard. For example, if the standard steel contains .4 per cent. carbon, and you wish to get the exact color for the .32 per cent. carbon tube in the permanent series, dissolve .2

* Chem. News, xxii. 101. † Ibid., xliv. 173.

gramme of the standard exactly as directed on page 167, pour the solution into a carbon tube, and dilute it in accordance with the formula, carbon required : carbon of standard :: 10 c.c. : the number of c.c. required, or, in this case, 32 : 40 :: 10 c.c. : 12.5 c.c. Therefore dilute the solution in the carbon tube to 12.5 c.c. pour 10 c.c. into a test-tube exactly like those used for the permanent standards, and compare it with the .32 per cent. carbon tube. If the color of the permanent solution is not exactly the same, correct it by adding portions of the solutions of the iron, cobalt, or copper salts, or water containing .5 per cent. hydrochloric acid. The iron salt or hydrochloric acid alone gives a yellowish, the cobalt salt a brownish, and the copper salt a greenish, tone to the solution. The standards may now be arranged in a rack, as shown in Fig. 84. The colors of the permanent standards once

FIG. 84.



fixed, the samples to be analyzed are treated exactly as described on page 167, the test-tubes used being precisely like those containing the permanent standards, and each one carefully graduated to contain 10 c.c. When the samples (.2 gramme each) are dissolved and cooled, dilute each solution in turn with cold water to 10 c.c., mix thoroughly, and compare it with the standards in the rack, by which means the carbon may be estimated to the nearest hundredth of a per cent.

In testing white cast iron, use only .05 gramme, dissolve in 7 c.c. nitric acid, dilute the standard to some convenient amount approximating 20 c.c., and compare as quickly as possible to avoid the precipitation of carbonaceous matter, which is apt to occur under these circumstances. The graphite in ordinary gray pig-iron, and sometimes even in steels, renders filtration necessary. In this case add to the cold acid solution one-half of its volume of water, filter through a small, dry, ashless filter into the carbon tube, wash with as little water as possible, and compare as usual.

DETERMINATION OF TITANIUM.

By Precipitation.

Only traces or very minute amounts of titanium are found in steel, but notable quantities exist in some kinds of pig-iron. As pointed out by Riley,* when pig-iron containing titanium is dissolved in hydrochloric acid a portion of the titanium goes into solution, while the remainder is found with the insoluble matter. The insoluble portion, as noticed page 80 *et seq.*, contains phosphoric acid. It is a curious fact that as titanic acid interferes with the determination of phosphoric acid by its tendency to form upon evaporation to dryness an insoluble phospho-titanate, so phosphoric acid interferes with the determination of titanic acid by partially preventing the precipitation of titanic acid from its boiling sulphuric acid solution. The best method, therefore, for the determination of titanium is to proceed exactly as for the determination of phosphorus when titanium is present, as directed on page 80 *et seq.*, until the residue from the aqueous solution of the sodium carbonate fusion is obtained. Dry this residue, transfer it to a large platinum crucible, preferably the one in which the sodium carbonate fusion was made, burn the filter, add its ash to the residue, and fuse the whole with fifteen or twenty times its weight of potassium bisulphate. In fusing with potassium bisulphate it is necessary to begin with a very low heat, and to raise the temperature very slowly and carefully to a low red heat, as the mixture has a strong tendency to boil over the top of the crucible whenever the temperature is increased too rapidly. When the lid of the crucible is raised, fumes of sulphuric anhydride should come off, and the fusion should be kept at this point for several hours, or until it is quite clear and the whole of the ferric oxide has been dissolved. Allow the fused mass to cool, add to it from 5 c.c. to 10 c.c. of strong sulphuric acid, and heat until it is perfectly liquid. When cold it will remain liquid. Pour it carefully into 400 c.c. of cold water in a 600 c.c. beaker. Add a little hydrochloric acid if necessary and 50 c.c. of strong sulphurous acid, or 5 c.c. of ammonium bisulphite. Filter into an 800 c.c. beaker, add ammonia until a permanent preciptate forms,

* Jour. Chem. Soc., xvi. 387.

redissolve with a few drops of hydrochloric acid, add a filtered solution of 20 grammes of sodium acetate and one-sixth the volume of the solution of acetic acid (1.04 sp. gr.), and heat to boiling. The titanic acid is precipitated almost immediately in a flocculent condition and quite free from iron. Boil for a few minutes, allow the titanic acid to settle, filter, wash with hot water containing a little acetic acid, dry and ignite. Fuse the precipitate with a small amount of potassium bisulphate. Dissolve in water with a few drops of hydrochloric acid and pass hydrogen sulphide through the solution to precipitate any small amount of platinum that may be present (from the crucible). Filter and precipitate as before. Filter, ignite and weigh as TiO_2 which contains 60.05 per cent. titanium.

By Volatilization.

Drown * suggested the method of determining titanium by volatilizing it in a current of chlorine gas. The details, with some modifications, are as follows: Treat the sample exactly as directed for the determination of silicon, *by volatilization in a current of chlorine gas, page 70 et seq.*

To the filtrate from the silica (page 72) add a slight excess of ammonia, acidulate with acetic acid, boil, filter, wash, and ignite the precipitate. As this precipitate may contain a little ferric oxide (carried over mechanically as ferric chloride), phosphoric acid, tungstic acid, etc., fuse it with a little sodium carbonate, dissolve the fused mass in hot water, filter, wash, dry, and ignite the residue, which will contain all the titanic acid as sodium titanate, and any iron that may have been present as ferric oxide. The filtrate will contain the phosphoric acid, etc. Fuse the ignited residue with a little potassium bisulphate, treat it in the crucible with strong sulphuric acid, as directed on page 172, and determine the titanic acid in the manner there described.

DETERMINATION OF COPPER.

For the determination of copper the precipitate by hydrogen sulphide, obtained in the determination of phosphorus (page 77), may not be used, as some of the copper will have been volatilized by the evaporations to dryness.

* Trans. Inst. Min. Engineers, viii. 508.

Dissolve 10 grammes of drillings in a 600 c.c. beaker in 40 c.c. hydrochloric acid, or 20 c.c. strong sulphuric acid and 100 c.c. water. Boil until all the iron is dissolved, add to the solution 250 c.c. cold water, add ammonia until a slight permanent precipitate appears, dissolve this precipitate with a few drops of hydrochloric acid, add 5 c.c. of the acid and pass hydrogen sulphide through the solution. Heat the solution to boiling and then allow it to cool while the gas is passing. Filter, wipe any adhering precipitate from the beaker and tube with filter paper and wash thoroughly with water containing a little hydrochloric acid and saturated with hydrogen sulphide. Dry and ignite the filter and precipitate in a porcelain crucible, burn off all the carbon from the paper, allow the crucible to cool and digest the precipitate at a gentle heat with nitric acid and a few drops of sulphuric acid, keeping the crucible covered with a small watch glass. When the copper sulphate is entirely dissolved, remove the watch glass and evaporate the solution until fumes of sulphuric anhydride are given off. Dissolve in water and precipitate the copper by electrolysis. Instead of using hydrogen sulphide the copper may be precipitated in a sulphuric acid solution by sodium thiosulphate. Dissolve in sulphuric acid as before directed, dilute to boiling and add 3 grammes of sodium thiosulphate dissolved in 10 c.c. hot water. Boil for a few minutes, filter, wash with water and determine the copper as before directed.

Pig Iron.

The copper dissolves in hydrochloric acid when the pig iron is boiled thoroughly in the acid, but it is necessary to filter from the silica and graphite before precipitating with hydrogen sulphide. When sulphuric acid is used as the solvent, after filtering off the insoluble material, dry and ignite it, treat it with hydrofluoric and sulphuric acids, heat until the sulphuric acid fumes freely, cool, dissolve in water and add to the filtrate. Then proceed as in the case of steels.

Instead of determining the copper by electrolysis, it may be determined as cuprous sulphide, Cu_2S. To determine it as cuprous sulphide, dilute the sulphate obtained by any of the methods mentioned above with water to about 50 c.c., add an excess of ammonia, filter from ferric

oxide, etc., wash with ammoniacal water, and pass hydrogen sulphide through the cold solution. Filter, wash with hydrogen sulphide water, dry the filter and precipitate, transfer the latter to a small porcelain crucible, burn the filter, and add its ash to the precipitate. Add to the precipitate in the crucible about twice its volume of flowers of sulphur and ignite it in a current of hydrogen, as directed for the determination of manganese as MnS, page 107. Weigh as cuprous sulphide, which contains 79.87 per cent. copper.

DETERMINATION OF NICKEL AND COBALT.

The Acetate Method.

Treat 3 grammes of the drillings exactly as directed for the determination of manganese by the acetate method (page 103 *et seq.*). The precipitate by hydrogen sulphide (page 105) will contain all the nickel and cobalt and a portion of the copper contained in the sample. Filter this precipitate on a small washed filter, wash with hydrogen sulphide water containing a little free acetic acid, dry and ignite the filter and precipitate, and transfer them to a small beaker. Dissolve in hydrochloric acid with a few drops of nitric acid, evaporate to dryness, redissolve in from 10 to 20 drops of hydrochloric acid, dilute with hot water to about 50 c.c., heat the solution to boiling, and pass a stream of hydrogen sulphide through the boiling solution to precipitate any copper that may be present. Filter, wash with hot water, evaporate the filtrate to dryness, moisten the dry mass with 4 or 5 drops of hydrochloric acid, add 20 or 30 drops of cold water and then 2 or 3 grammes of potassium nitrite (KNO_2)* dissolved in the least possible amount of water and acidulated with acetic acid. The presence of cobalt is shown by the formation of a bright yellow precipitate of potassium-cobalt nitrite, $(KNO_2)_6CO_2(NO_2)_6 + Aq$. Stir the solution, and allow it to stand twenty-four hours, with occasional stirring. Filter on a small ashless filter, wash with water containing potassium acetate and a little free acetic acid, remove the filtrate which

* See page 43.

contains the nickel, and wash the precipitate and filter free from potassium acetate with alcohol. Ignite the filter and precipitate carefully in a porcelain crucible, being careful not to raise the temperature high enough to fuse the precipitate; transfer to a very small beaker, and digest in hydrochloric acid and a little potassium chlorate. Evaporate to dryness, redissolve in from 3 to 5 drops of hydrochloric acid, dilute with cold water, add about 1 gramme of sodium acetate, and boil for an hour to precipitate the small amount of ferric oxide and alumina that is always present. Filter, to the filtrate add excess of ammonia and ammonium sulphydrate, and heat to boiling. As soon as the preciptate of cobalt sulphide has settled, filter, wash with water containing a little ammonium sulphydrate, dry, and ignite the precipitate and filter in a platinum crucible. When all the carbon is burned, allow the crucible to cool, pour in a little nitric acid, heat carefully, and finally evaporate to dryness. Add a few drops of sulphuric acid, digest until the sulphide and oxide are changed to cobalt sulphate, drive off the excess of sulphuric acid, heat finally to dull redness for a few moments, cool, and weigh as cobalt sulphate, $CoSO_4$, which contains 38.04 per cent. of cobalt. Heat the filtrate from the potassium-cobalt nitrite to boiling, add a slight excess of caustic potash, boil for a few minutes, filter, and wash the precipitate of nickel oxide with hot water. Dissolve the precipitate on the filter with hydrochloric acid, allow the solution to run back into the beaker in which the nickel oxide was precipitated, and wash the filter with hot water. Evaporate the solution to dryness, redissolve in from 3 to 5 drops of hydrochloric acid, dilute with cold water to about 50 c.c., add 1 gramme of sodium acetate, boil for an hour, filter off any ferric oxide and alumina, and wash with hot water. To the filtrate add an excess of ammonium sulphydrate (a brown color shows the presence of nickel), acidulate with acetic acid, heat to boiling, and pass a current of hydrogen sulphide through the boiling solution until the precipitated sulphur and nickel sulphide agglomerate. Filter, wash with hydrogen sulphide water, dry, and ignite the filter and precipitate. Allow the crucible to cool, add a little ammonium carbonate to the precipitate, heat to dull redness, and volatilize any sulphuric acid that may have been formed as ammonium

sulphate, cool, and weigh as nickel sulphide or nickel oxide, which contains 78.58 per cent. of nickel. The nickel and cobalt may also be weighed in the metallic condition by precipitating them by the battery from the ammoniacal solutions of the sulphates. If it is not desired to separate them, evaporate the filtrate from the precipitated copper sulphide with an excess of sulphuric acid until the hydrochloric acid is driven off and fumes of sulphuric anhydride appear, allow the beaker to cool, add about 5 c.c. water, then an excess of ammonia, filter if necessary, and precipitate on a small cylinder in a strongly ammoniacal solution. Wash the cylinder with water, then with alcohol, dry at 100° C., and weigh as nickel and cobalt. To determine the nickel and cobalt separately, precipitate the cobalt as potassium-cobalt nitrite, treat the ignited cobalt precipitate with an excess of sulphuric acid, heat until fumes of sulphuric anhydride are given off, dilute a little, make the solution strongly ammoniacal, and precipitate the cobalt as above directed. Precipitate the nickel oxide, in the filtrate from the cobalt, by caustic potash solution, filter, wash, dissolve on the filter in hydrochloric acid, evaporate the solution with sulphuric acid, add excess of ammonia, and precipitate the nickel by the battery as above.

For the analysis of nickel steel, which contains from 2 to 3 per cent. of nickel, use 1 gramme of the sample, and, after obtaining the precipitate of nickel sulphide as described above, burn it with the filter in a porcelain crucible, allow it to cool, add a little pure powdered sulphur, and ignite in a stream of hydrogen gas as described on page 107. Weigh as nickel sulphide.

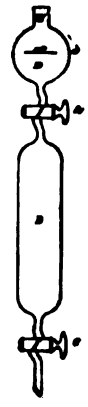
The Ether Method.

This method of separation, due to J. W. Rothe,* is founded on the fact that ether will take from an aqueous hydrochloric acid solution nearly all the ferric chloride, leaving in the solution the chlorides of nickel, cobalt, aluminum, chromium, manganese, and copper. The method is given in considerable detail by Prof. Ad. Carnot in his "Methodes d'Analyse des Fontes, des Fers, et des Aciers," 1895, p. 123 *et seq.*

* Mittheilungen aus den Königlich Tech. Versuchsanstatten zu Berlin, 1892, Part iii.

Dissolve from 2* to 5 grammes of the drillings in a 250 c.c. beaker in aqua regia. Evaporate to dryness to render silica insoluble, redissolve in hydrochloric acid, dilute slightly, filter, and evaporate the filtrate to syrupy consistency. The success of the separation depends largely upon the specific gravity of the solution, as a solution of the density 1.100 to 1.105 saturated with ether retains the smallest amount of ferric chloride. The tube shown in Fig. 85, suggested by Carnot, is admirably adapted for the treatment with ether.† It consists of a bulb, B, of 200 c.c. capacity, about 20 cm. (8 inches) high and 3.5 cm. (1.5 inches) wide, with a tube at either end 3 mm. (⅛ inch) internal diameter, carrying the stopcocks A and C. The upper one connects with a bulb, D, of 100 c.c. capacity, with a mark at *m* to show when the bulb contains 30 c.c.

FIG. 85.



Close both stopcocks, pour a few drops of ether into the upper bulb, open A to allow the ether to run into B. Close A, warm the bulb B with the hand, and open and close C. This will create a partial vacuum in B. Transfer the solution from the beaker to the bulb D, washing it out of the beaker with hydrochloric acid of 1.1 sp. gr. and filling D to the mark *m*. This strength of hydrochloric acid gives the solution, after the separation of the ferric chloride of ether, a sp. gr. of 1.100. Stand the tube in a vessel of cold water, open A and allow the solution to run into B. Close A and fill the bulb D with ether. Allow the ether to flow slowly into B so that it forms a separate layer over the hydrochloric acid solution. Mix the two liquids gradually by giving the apparatus a circular motion, replacing it in the cold water from time to time so as to avoid a rise in the temperature, which would cause a reduction by the ether of some of the ferric chloride. Finally close A, shake the tube well, open A to relieve the pressure, return the tube to the water, and allow it to stand some minutes to give the liquids the opportunity to separate. The upper stratum is the ethereal solution of the ferric chloride and the lower the

* For nickel steel containing from 2 per cent. to 3 per cent. of nickel 2 grammes are sufficient.

† The separatory funnels shown in Fig. 88 may be used.

hydrochloric acid solution of the other metals, with usually about 1 per cent. of the ferric chloride. Open the stopcock C, allow the lower solution to run into a small beaker, close C, and wash the end of the tube with a little water. Introduce about 10 c.c. of hydrochloric acid (1.1 sp. gr.) into the bulb D, allow it to run into B, close A, shake the apparatus and allow it to stand for a few minutes. Allow the lower liquid to run into the beaker, which will now contain all the nickel, cobalt, etc., that were in the steel.* One separation with ether is generally sufficient, but if it is considered desirable to remove still more of the iron, run the solution and washings into the bulb of another tube like the one described instead of into a beaker, and repeat the treatment with ether.

Heat the solution in the beaker to drive off the ether dissolved in it, add bromine or a little hydrogen peroxide and excess of ammonia, boil, and filter. Redissolve the precipitate and repeat the operation, adding the two filtrates together. The filtrates contain all the nickel, cobalt, and copper, while the insoluble matter contains, besides ferric hydrate, any alumina and chromium sesquioxide that may have been in the steel. Acidulate the filtrate with hydrochloric acid, adding about 5 per cent. of its volume in excess, and precipitate the copper with hydrogen sulphide. Filter and wash. To the filtrate add an excess of ammonia, then a few c.c. of ammonium sulphydrate, acidulate with acetic acid, and pass hydrogen sulphide through the boiling solution. Filter and wash the precipitate of sulphur and nickel and cobalt sulphides. Test the filtrate by adding an excess of ammonia, and if it darkens repeat the precipitation with ammonium sulphydrate, acetic acid, and hydrogen sulphide. In the case of nickel steel, cobalt is generally disregarded, and the precipitate is ignited and weighed after treatment with ammonium carbonate as nickel oxide, NiO.

Or, heat the liquid separated from the ethereal solution to drive off the ether, dilute slightly, pass hydrogen sulphide to precipitate the

* To recover the ether, dilute it in the tube with an equal volume of water, shake the tube and allow it to stand. The ether rises to the top and the aqueous ferric chloride solution remains below. Draw off the latter and distil the ether from caustic lime.

copper, filter, and wash. Boil the solution to expel the dissolved gas, add bromine to oxidize the iron, and precipitate two or three times with ammonia to get rid of the iron. Acidulate the solution with acetic acid and pass hydrogen sulphide through the boiling solution for fifteen or twenty minutes, extinguish the light, and pass the hydrogen sulphide for fifty or twenty minutes longer, filter off the nickel sulphide and ignite it. Return it to the beaker in which the precipitation was made and dissolve it with any precipitate that adhered to the beaker and evolution tube in hydrochloric acid with the addition of a little nitric acid, transfer to a smaller beaker, add two c.c. of strong sulphuric acid and evaporate until fumes of sulphuric acid are given off. Cool, dilute, heat until the nickel sulphate is dissolved, add an excess of ammonia, and precipitate on the battery as metallic nickel and cobalt.

To separate the nickel and cobalt, dissolve the ignited precipitate of the sulphide obtained above in hydrochloric acid with a little nitric acid, evaporate to very small bulk, and separate with potassium nitrite as described on page 175.

Volumetric Method.

Instead of precipitating the nickel electrolytically, it may be determined volumetrically by a standard solution of potassium cyanide. The method is based on the fact that in a solution of nickel chloride containing a slight excess of ammonia and a small amount of silver iodide, the opalescence caused by the silver iodide disappears in the presence of an excess of potassium cyanide. The addition of potassium cyanide to such a solution causes the formation of potassium nickel cyanide until all the nickel present has been converted, after which an excess of potassium cyanide changes the precipitated silver iodide into soluble potassium silver cyanide, causing the solution to clear.

It is necessary of course to get rid of the iron, and the quickest and most satisfactory method of accomplishing this is to separate it by ether. The details of this method have been carefully worked out by Sargent (*Journal of the American Chemical Society*, vol. xxi, p. 854) and are essentially as follows: Treat two grammes of steel by the ether method, page 177, until the solution containing the nickel, etc., and a

small amount of iron is obtained. Boil off the ether and evaporate the solution to 15 c.c. or 20 c.c., dilute to 100 c.c. with hot water, precipitate the copper by hydrogen sulphide and filter. Boil the filtrate to expel the hydrogen sulphide, add an excess of bromine and precipitate the iron and manganese by ammonia, filter, dissolve the precipitate in hydrochloric acid and repeat the operation. As the amount of iron is small, two separations should be sufficient to obtain all the nickel in the filtrates. Evaporate the filtrates to about 100 c.c., carefully neutralize by hydrochloric acid, and add 1 c.c. of ammonia in excess. Transfer the solution to an Erlenmeyer flask and cool it. Add 5 c.c. of a solution of silver nitrate and the same amount of a solution of potassium iodide, which will produce a decided opalescence. Run in a standard solution of potassium cyanide until the solution clears. A dark background is best, as it shows the clearing of the solution and makes the end reaction very sharp.

Standard Solutions.

Silver nitrate: .5 gramme silver nitrate to the litre of water.

Potassium iodide: 20 grammes potassium iodide to the litre of water.

Potassium cyanide: 4.6 grammes pure potassium cyanide to the litre of water. This solution may be standardized by using a nickel steel in which the nickel has been carefully determined by electrolysis, or a solution may be made of a pure nickel salt such as the sulphate to contain about 1.6 grammes of nickel to the litre. Determine the nickel accurately and then measure 50 c.c. of the solution into a flask, add 1 c.c. of ammonia in excess, 5 c.c. of the silver nitrate, and 5 c.c. of the potassium iodide solutions, dilute to about 100 cc., and titrate. Take 5 c.c. of the silver nitrate solution, 5 c.c. of the potassium iodide solution, and 5 or 10 grammes of ammonium chloride, dilute to 100 c.c., add 1 c.c. in excess of ammonia, and titrate with the potassium cyanide solution. This gives a correction which must be applied to all titrations. Subtract this correction from the number of c.c. used in standardizing the potassium cyanide solution and divide the weight of nickel taken by this corrected reading. The result is the value in metallic nickel of one c.c. of the potassium cyanide solution.

In chrome nickel steels the chromium is precipitated with the ferric oxide, and when the amount of manganese is not large it will be practically eliminated by adding bromine or a little ammonium persulphate to the solution before precipitating by ammonia. Mr. Kopp, of the Midvale Steel Company, informs me that their experience at Midvale has been that in vanadium-chrome steel the vanadium was all carried down by the sesquioxide of chrome when this was precipitated by ammonia. If manganese is present in the solution when it is titrated the results of course would be affected. The titration method is a little shorter than the electrolytic method and when many determinations are made in a day its use becomes almost obligatory.

When working on samples of unknown composition it is necessary to precipitate the copper by hydrogen sulphide; but when the amount of copper is very small it may be disregarded; or when the amount is known the proper allowance may be made and the hydrogen sulphide precipitation omitted.

PRECIPITATION BY DIMETHYLGLYOXIME AND TITRATION WITH CYANIDE.

By Dr. H. L. FREVERT.

Dissolve one gramme of the sample in 50 c.c. of nitric acid, 1.13 sp. gr., in a 400–500 c.c. beaker. Chrome nickel steels with one per cent. or more of chromium after certain heat treatments, when dissolved in dilute nitric acid liberate a complex carbide which gives the solution a distinct turbidity. In such cases it is best to dissolve one gramme of the sample in 60 c.c. of sulphuric acid, 1.22 sp. gr., and then oxidize with excess of dilute nitric acid and boil until a clear solution is obtained.

Add 25 c.c. of citric acid solution (50 grammes citric acid dissolved in 100 c.c. of water) and then make the solution slightly but distinctly ammoniacal, and allow it to become thoroughly cool. Time may be saved by adding clean, clear ice directly to the solution.

The nickel is now precipitated as nickel glyoxime by the gradual addition with vigorous stirring of a one per cent. dimethylglyoxime

alcoholic solution. "Denatured" or "wood" alcohol as a solvent for the dimethylglyoxime introduces no error and effects a considerable economy. Twenty c.c. of a one per cent. solution are sufficient to precipitate the nickel in one gram of a four per cent. nickel steel and the solution may be used accordingly.

The nickel glyoxime is separated by filtration with suction through an asbestos filter * one-eighth inch in thickness, formed on a perforated porcelain plate in an ordinary funnel. Wash the precipitate four or five times with water and then transfer the funnel with the precipitate to a clean eight-ounce suction flask. Dissolve the precipitate on the filter with 10 to 20 c.c. of hot concentrated nitric acid, added drop by drop, and then wash four or five times with water; the process being conducted with suction. The nickel solution is then poured into the beaker in which the precipitation was made, three grammes of ammonium persulphate added and the solution is boiled for 3 to 5 minutes. The solution should be perfectly clear at this point, but if any turbidity persists, the solution should be filtered, an asbestos filter and suction being most convenient. Clean, clear ice may be added to cool the solution, which is then made slightly but distinctly ammoniacal and 10 c.c. each of silver nitrate and potassium iodide solutions are added as indicator and titration is conducted with a standardized cyanide solution.

Solutions for Titration.

Silver nitrate—0.5 gram $AgNO_3$ in 1000 c.c. water.

Potassium iodide—20 grams KI in 1000 c.c. water.

Cyanide—approximately 4.57 grams of KCN in 1000 c.c. water. This solution is standardized against a steel of known nickel content and its concentration varied so that 1 c.c. = 0.10 per cent. Ni.

With a little practice on this method, the nickel in a sample of steel may be determined accurately in from 20 to 25 minutes. In chrome nickel steels and for determination of small amounts of nickel in steels and iron, this method is especially valuable.

* Or an alundum plate

PRECIPITATION BY DIMETHYLGLYOXIME AND WEIGHING AS METALLIC NICKEL.

For nickel steels dissolve 1 gramme and precipitate as directed above. Filter (the alundum plate as described on page 25 is admirable for this purpose), wash, and transfer the filter to the arrangement shown in Fig. 17. Dissolve the nickel glyoxime in dilute hot nitric acid, allowing the solution to run into a 400 c.c. beaker, and wash thoroughly with hot water. Add 5 c.c. strong sulphuric acid and evaporate until the sulphuric acid fumes freely. Cool, dilute with cold water, add an excess of ammonia, and precipitate by electrolysis, using the rotating anode or double cylinders with a stirring device.

PRECIPITATION AND WEIGHING AS NICKEL GLYOXIME

In ordinary steels containing small amounts of nickel it is best to use 2 grammes of the sample, and proceed as above until the precipitate of nickel glyoxime shall have been dissolved in nitric acid. To this solution, which should not exceed in volume 100 c.c., add a crystal of citric acid, a slight excess of ammonia, and a few c.c. of the solution of dimethylglyoxime. Stir well and after half an hour filter the precipitate on a Gooch crucible, wash with cold water, dry at 100° C., and weigh as nickel glyoxime, $Ni(C_4H_7N_2O_2)_2$, which contains 20.314 per cent. of nickel. When the metal is present in only very small amounts it is generally necessary to allow the solution containing the first precipitate of nickel glyoxime to stand over night after stirring vigorously at intervals.

When much cobalt is present this method cannot be used, as the cobalt prevents the precipitation of the nickel as glyoxime.

DETERMINATION OF CHROMIUM

All chrome steels are soluble in hydrochloric acid or in aqua regia, leaving occasionally a residue which may contain small amounts of chromium. For gravimetric determinations a preliminary separation of the greater part of the iron is practically a necessity, and Rothe's method for accomplishing this is unequalled both for accuracy and speed.

The Ether Method.

Treat from 1 to 5 grammes of the steel exactly as described for the determination of nickel by the ether method (page 179), until the precipitate by ammonia, consisting of ferric oxide, chromium sesquioxide, and manganese oxide, is obtained. Dry and ignite the precipitate. Fuse about 5 grammes of sodium carbonate in a 20 c.c. crucible, hold it firmly in the tongs, and by a rotary movement run the fused mass around until the bottom and the sides about two-thirds of the way up are, when cold, coated with the material. Place about half a gramme of sodium peroxide in the crucible, transfer the ignited precipitate to it, cleaning out any adhering particles with from half a gramme to 1 gramme of the peroxide. Mix thoroughly with a platinum wire and heat over a low light. The sodium peroxide fuses quietly; as soon as it is perfectly liquid run it up on the lining of fused sodium carbonate and allow it to cool. Stand the crucible in a dry 400 c.c. beaker and add a little cold water from a wash bottle. The undecomposed sodium peroxide effervesces violently, but by stirring it with a rod the liquid may be prevented from going over the side of the crucible. When the addition of a small amount of water causes no further action, remove the crucible from the beaker and wash the contents into it with a spray of hot water. Dilute to 100 c.c. with hot water and boil vigorously for 15 to 20 minutes to decompose all the sodium peroxide. Particles of the ignited precipitate may remain with some sodium peroxide adhering to the sides of the first crucible. Heat this gently until the peroxide fuses, cool, dissolve in water, and add to the main solution. All the chromium is in solution as chromate, while ferric oxide, manganese oxide, and nickel oxide are precipitated. Filter, wash with hot water containing a little sodium carbonate, and to the filtrate add cautiously 10 c.c. of strong sulphuric acid which has been diluted with 30 c.c. of water and boiled. Boil the solution to get rid of the carbon dioxide and cool. To the cold solution, which should be about 400 c.c. in volume, add a weighed amount of ferrous ammonium sulphate and titrate with permanganate. The green color of the solution persists until nearly all the ferrous salt has been oxidized, and when the first purple tint appears the reaction is complete.

From the number of c.c. of permanganate corresponding to the weight of ferrous ammonium sulphate added is subtracted the number required to oxidize the amount unacted on by the chromic acid, and the remainder is the number of c.c. of permanganate equivalent to the amount of ferrous ammonium sulphate oxidized by the chromic acid. The reaction is 6 $FeSO_4(NH_4)_2SO_4$, $6H_2O + 2CrO_3 + 6H_2SO_4 = 3Fe_2(SO_4)_3 + 6(NH_4)_2SO_4 + Cr_2(SO_4)_3 + 42H_2O$ or one equivalent of chromic acid will oxidize 3 equivalents of ferrous ammonium sulphate to the ferric salt. Therefore, the value of the permanganate in metallic iron being known and the ferrous ammonium sulphate having been standardized by the permanganate, the amount of chromium is calculated as follows:

3 equiv. iron = 167.52 : 1 equiv. chromium = 52:: the value of the ferrous ammonium sulphate oxidized by the chromic acid, in iron : its value in chromium; or multiply the iron value of the ferrous ammonium sulphate oxidized by the chromic acid by $\frac{52.}{167.52} = .31041$.

When the amount of chromium present in the steel is very small it may be determined by color. Fuse the small precipitate of ferric oxide and chromic oxide in a lined crucible with a little sodium peroxide, as described above, dissolve the fused mass in a few c.c. of water, boil, and filter, using a small filter paper.

Receive the filtrate and washings, which should not exceed 40 or 50 c.c. in volume, in a tall 60 c.c. beaker and cool. Take another beaker of the same size, place in it 1 gramme of sodium carbonate and a little less water than the volume of solution in the first beaker, and add to it a sufficient amount of a standard solution of potassium dichromate to match the color of the solution in the first beaker. The standard solution is prepared as follows:

Dissolve 0.0283 gramme of potassium dichromate in 100 c.c. water, 1 c.c. of this solution contains 0.0001 gramme chromium.

The Volumetric Method.

Galbraith * has suggested a rapid method for the determination of chromium when it is present in appreciable amounts, as in chrome steel or

* Chem. News, xxxv. 151.

chrome pig-iron. Dissolve from 1 to 3 grammes of the sample in dilute sulphuric acid (1 part sulphuric acid and 6 parts water), add potassium permanganate in crystals until the iron is all oxidized and the liquid is quite red in color, then add as much more to oxidize the chromium to chromic acid. Heat the solution to boiling, and boil until the permanganate is all decomposed and there remains a precipitate of manganese oxide. Filter, wash with hot water, to the filtrate add a measured volume of standardized ferrous sulphate, and determine the excess of ferrous sulphate by a standard solution of permanganate. From the amount of ferrous sulphate oxidized by the chromic acid calculate the amount of chromium as shown on page 186.

Barba's Modifications.

Barba * has suggested several modifications which decidedly improve the method. To avoid the large precipitate of manganese dioxide, he uses nitric acid to oxidize the iron, having found that even a considerable excess of this reagent does not affect the subsequent reactions. He uses, most successfully, ammonia to destroy the excess of potassium permanganate. The method is as follows:

Dissolve 1.25 grammes steel in 20 c.c. sulphuric acid (1.2 sp. gr.). When solution is complete, add nitric acid drop by drop until the iron is oxidized; 5 c.c. of nitric acid (1.2 sp. gr.) is generally sufficient.

Boil to remove nitrous fumes, and add hot water to bring the volume to 150 c.c.; add from a pipette 5 c.c. of a saturated solution of potassium permanganate and boil briskly for from fifteen to twenty minutes; remove from the plate, wash down the sides of the beaker to remove all permanganate, and add 25 c.c. strong ammonia down the side of the beaker; shake well, and replace on the cooler part of the plate to avoid "bumping," of which there is some danger if the heat be raised too rapidly. Shake occasionally and digest for about fifteen minutes, or until the permanganate is all decomposed, then add cautiously 20 c.c. dilute sulphuric acid (1.58 sp. gr.) and bring gently to boiling. Cool the solution and pour into a graduated 250 c.c. flask. Make up to mark with cold

* The Iron Age, lii. 153.

water, and mix well by pouring back and forth into a dry beaker a few times. Allow the precipitate to settle, and filter through double, close, hard, dry filters, into a dry beaker; measure off 200 c.c. (equal to 1 gramme sample) of the clear filtrate, titrate by adding a known excess of ferrous sulphate, and determine the excess by standard permanganate.

Frevert's Modifications.

Dissolve a 1 gramme sample in 65 c.c. of hot sulphuric acid, 1.22 sp. gr., in a 250–300 c.c. beaker. When the sample is completely in solution, oxidize the boiling solution with nitric acid, 1.13 sp. gr., added drop by drop, and then one to two c.c. in excess. The carbides in certain heat treated chrome nickel steels are not decomposed immediately by nitric acid. These carbides always contain chromium and it is essential that they be completely decomposed. In such cases, boil the solution until fumes of sulphuric acid are evolved and dilute the solution to a volume of 70 c.c. If black particles of carbide still persist, the operation is repeated. In tungsten steels, the tungstic oxide precipitated by oxidation with nitric acid is at first greenish yellow in color, certain evidence of undecomposed carbides containing chromium. Here again these carbides must be decomposed by boiling until the tungstic oxide is of a bright yellow color.

The solution is now diluted if necessary, so that its volume is about 70 c.c., brought to boiling, and removed from the hottest portion of the hot plate. One to four grammes of specially prepared lead peroxide are added and the solution is boiled vigorously for 2 to 4 minutes. The amount of lead salt to be added varies with the composition of the sample, and when sufficient is present the mixture has a dark reddish brown color while boiling. If any manganese is present, the color of the permanganic acid should be distinct.

While the oxidation with the lead is taking place, the mixture to reduce the permanganic acid is prepared by mixing 140 c.c. of a manganese sulphate solution containing 1 gramme of $MnSO_4 4H_2O$, and 20 c.c. of concentrated ammonia, .90 sp. gr. The oxidized solution is now

removed from the hot plate, stirred and the freshly precipitated manganese hydroxide mixture is added in a slow stream with *constant* stirring. Allow the mixture to stand for two minutes and then filter with suction into a flask containing 25–30 c.c. of sulphuric acid, 1.56 sp. gr., using an asbestos felt on a perforated porcelain plate in a large funnel, and wash the filter three or four times with water. It is essential that during filtration the filter be kept covered with liquid; otherwise, the oxidizing action of the air drawn through the paste containing the lead salt and oxides of manganese will form permanganic acid which will be washed into the flask. The funnel above the filter may be filled with small pieces of ice during filtration, so that with the exception of vanadium steels, the filtrate is cool enough to titrate immediately. To solutions containing vanadium, ice should be added, or the solution should be cooled by surrounding it with ice and ice water immediately preceding titrating with permanganate.

The chromium is determined by the reduction of the chromate with excess of ferrous sulphate and titration of the excess with standardized potassium permanganate according to the well-known procedure. The end point of the titration is the disappearance of the green color and *first* appearance of the most delicate pink.

By this method an accurate determination of chromium in ordinary chrome and chrome nickel steel, when hot sulphuric acid is used as a solvent, may be completed in fifteen minutes.

Special Lead Dioxide.

Powder 1 kilo of C. P. red lead free from manganese and chlorides and sift through a 60–80 mesh sieve into a two litre jar half filled with distilled water. It is best sifted by simply jarring the sieve. Stir thoroughly and while stirring pour in a thin stream of dilute nitric acid, 1 part 1.42 acid to 12 parts water, until the jar is filled. Allow the lead oxide to settle and syphon off the clear liquid. Add more of the dilute acid with constant stirring until the equivalent of 175 c.c. of strong acid has been added. Wash thoroughly by decantation, filter on a layer of asbestos on a filter plate, dry and powder.

DETERMINATION OF ALUMINUM

Stead's Method.*

Weigh 6, 12, or 24 grammes steel, place in a 600 c.c. beaker, cover with a watch-glass, dissolve in hydrochloric acid (strong), evaporate to dryness, redissolve in hydrochloric acid, filter into a 1000 c.c. beaker through an ashless filter, nearly neutralize the filtrate with dilute ammonia, and boil. The filtrate should measure 500 or 600 c.c. Add to the solution 1 or 2 c.c. of saturated solution of ammonium phosphate, and then a large excess of sodium hyposulphite, boil till all sulphurous acid has passed off (half an hour's boiling should be sufficient); just before filtering add 20 c.c. of a saturated solution of ammonium acetate, stir to mix, and filter through an ashless filter, wash precipitate and filter five or six times, add to the beaker in which the precipitate had been formed 10 c.c. hydrochloric acid, heat to boiling, remove the vessel containing the filtrate, and instead of it place under the funnel a platinum dish, and pour over the filter the boiling acid. Rinse out the beaker and wash all soluble matter on the filter with a fine jet, evaporate the solution to dryness in the platinum dish, and heat to a temperature of 300° or 400° F. on the hot plate to drive off excess of acid.

Add from 2 to 5 grammes pure sodium hydrate made from sodium free from aluminum and about 2 c.c. water. Heat gently over a rose-burner for ten minutes, maintaining the mass in a fluid state all the time. Cool and add water, and boil till solution is complete. Make the bulk of the solution to 300 c.c. and note the temperature exactly. Shake well and filter through an ashless filter. Measure off 250 c.c. at the original temperature, equal to 5, 10, or 20 grammes steel. If any yellow tint is observable chromium may be present. In this case the aluminum phosphate must be neutralized with hydrochloric acid and precipitated by ammonium carbonate, taking care to boil the solution well to free from excess of ammonia before filtering. Filter through an ashless filter, dry, burn, and weigh, dissolve the precipitate in hydrochloric acid and determine phosphoric acid in it, and deduct the weight found from the weight of the original precipitate. If chromium is absent, neutralize the solution

* Prepared by Mr. J. E. Stead, of Middlesboro', England, for this volume.

with hydrochloric acid as before described, boil, and add excess of sodium hyposulphite, and boil for half an hour, filter off the precipitate, burn, and weigh as pure aluminum phosphate, which contains 22.18 per cent. of aluminum.

Carnot's Method.*

M. Carnot states that the method is very similar to that published by Mr. J. E. Stead in the *Journal of the Society of Chemical Industry*, 1889, page 965, but that he had used and taught it in the École des Mines for eight years. It is founded on the reaction that he pointed out in 1881, that aluminum is precipitated as the neutral phosphate from a boiling solution faintly acid with acetic acid. The precipitation succeeds equally well when the solution contains iron, if the ferric salt has been previously reduced to ferrous by sodium hyposulphite.

Treat 10 grammes of the iron or steel in a platinum dish covered with a piece of platinum-foil with hydrochloric acid, and when solution is complete, dilute and filter into a flask, washing the carbon, silica, etc., on the filter thoroughly with distilled water. Neutralize the solution with ammonia and sodium carbonate, but see that no permanent precipitate is formed, then add a little sodium hyposulphite, and, when the liquid—at first violet—becomes colorless, 2 or 3 c.c. of a saturated solution of sodium phosphate and 5 or 6 grammes of sodium acetate dissolved in a little water. Boil the solution about three-quarters of an hour, or until it no longer smells of sulphurous acid. Filter, and wash the precipitate of aluminum phosphate, mixed with a little silica and ferric phosphate, with boiling water. Treat the precipitate on the filter with hot dilute hydrochloric acid, allow the solution to run into a platinum dish, evaporate to dryness, and heat at 100° C. for an hour to render the silica insoluble. Dissolve in hot dilute hydrochloric acid, filter from the silica, dilute to about 100 c.c. with cold water, neutralize as before, add a little hyposulphite in the cold, then a mixture of 2 grammes of sodium hyposulphite and 2 grammes of sodium acetate, boil for one-half hour, wash, and weigh as aluminum phosphate, which contains 22.18 per cent. of aluminum.

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*A. Carnot, Moniteur Scientifique, 1891, p. 14.

Ether Method.

Treat 2 to 5 grammes of steel as described for the determination of nickel and evaporate the hydrochloric acid solution, which may contain nickel, chromium, copper, etc., until the ether is driven off, add a few drops of nitric acid or bromine to oxidize the iron, and precipitate by ammonia. Boil for a few minutes, filter, and wash; redissolve in hydrochloric acid, and reprecipitate, filter, and wash with boiling water. The precipitate will contain only iron, aluminum, and chromium. When chromium is absent, dissolve the precipitate in hydrochloric acid, evaporate to dryness, dissolve in a few drops of hydrochloric acid, filter, and dilute with cold water to 100 c.c., add 2 or 3 c.c. of sodium phosphate, and proceed as in the second precipitation of aluminum phosphate by Carnot's method.

When chromium is present, fuse the precipitate of ferric oxide, alumina, and chromic oxide with sodium carbonate and a little sodium nitrate, dissolve in water, add ammonium nitrate, boil well, and filter. The chromic acid will be in the filtrate and the ferric oxide and alumina will be insoluble. Dissolve in hydrochloric acid and proceed as when chromium is absent.

PRECIPITATION BY PHENYLHYDRAZINE

Instead of using Carnot's method, the alumina may be precipitated by phenylhydrazine, suggested by Hess and Campbell, Jour. Amer. Chem. Soc., vol. xxi, (1899), page 776. Evaporate the solution from the ether separation to dryness, dissolve in hydrochloric acid, dilute, and filter to get rid of the silica. To the solution, which should be about 150 c.c. in volume, add ammonia until a slight permanent precipitate of oxide of iron is obtained. Redissolve this by adding hydrochloric acid drop by drop and then 2 to 3 drops of acid after the solution clears. Heat to boiling and add a few drops of ammonium bisulphite, which will decolorize the solution and cause it to smell of sulphurous acid. Add a few drops of phenylhydrazine, which should precipitate the alumina. Add a few drops more of phenylhydrazine and a little filter paper pulp, stir vigorously, and allow the precipitate to settle, which it will do in a few minutes. Filter at once and wash four or five times with

cold water, filling the filter each time and allowing it to drain thoroughly after each washing. Wipe any adhering precipitate from the beaker with a little filter paper and ignite this and the filter containing the precipitate and weigh as Al_2O_3 which contains 53.03 per cent. aluminum.*

Fuse the precipitate with a little sodium carbonate dissolved in dilute nitric acid and test for phosphoric acid with molybdate solution. If any phosphoric acid is found, determine the amount and subtract from the Al_2O_3 before calculating the aluminum. If the solution of the sodium carbonate fusion is yellow in color, showing a small amount of chromium, it may be determined by color, as directed on page 186.

In chrome steels, after getting rid of silica as directed above, precipitate the oxide of iron, alumina, and chromic oxide by ammonia, filter and wash with hot water containing a little ammonium chloride or nitrate. Ignite the precipitate and fuse with sodium carbonate and potassium nitrate. Treat the fused mass with hot water, wash into a platinum dish, and boil, adding ammonium nitrate from time to time until the addition ceases to cause the liberation of ammonium carbonate. Evaporate to small bulk, add a drop or two of ammonia, dilute with hot water, and filter. The oxide of iron and alumina are precipitated and the sodium chromate is in the filtrate. Dissolve the precipitate in hydrochloric acid and precipitate by phenylhydrazine as directed above.

DETERMINATION OF ARSENIC.

By Distillation.

Lundin † has suggested the following method of determining arsenic, which gives very good results. Dissolve 10 grammes of drillings in a

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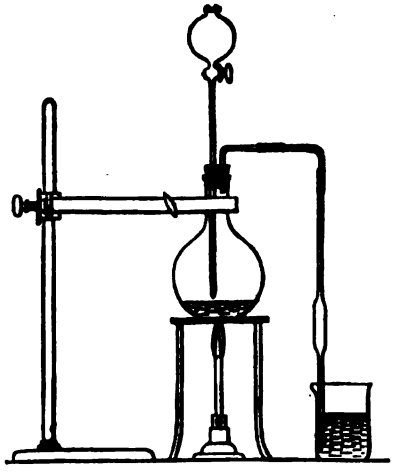
* Mr. Frederick Wynkoop found that by adding paper pulp to the solution the precipitated alumina could be washed thoroughly with cold water without danger of its dissolving. He found that very small precipitates could be entirely dissolved when the paper pulp was not used even by the sulphite phenylhydrazine wash water recommended by Hess and Campbell.

† Jern-Kontorets Annaler. 1883, p. 360; Chem. News, li. 115.

large beaker in nitric acid (1.2 sp. gr.), transfer the solution to a platinum or porcelain dish, add 25 c.c. sulphuric acid, and evaporate until copious fumes of sulphuric acid are given off. Cool the dish, add 50 c.c. of water, and evaporate again until the excess of sulphuric acid is driven off, and the ferric sulphate is so dry that it can readily be transferred to a flask of about 500 c.c. capacity. Add to the mass in the flask 15 grammes finely powdered ferrous sulphate, pour in 150 c.c. strong hydrochloric acid, and close the flask with a stopper carrying a tube bent twice at right angles and connected by a rubber tube with a 50 c.c. pipette, the point of which dips about ½ inch (12 mm.) into 300 c.c. of water in a beaker, as shown in Fig. 86. Heat the liquid in the flask gradually until it boils, and continue the distillation until the wide part of the pipette becomes heated. The arsenic acid in the solution is reduced by the ferrous sulphate, and, in the strong hydrochloric acid solution, is distilled over as arsenious chloride. Remove the light, disconnect the pipette, heat the solution in the beaker to about 70 ° C., and pass a rapid current of hydrogen sulphide through it until it is completely saturated. Remove the excess of hydrogen sulphide by a current of carbonic acid, and when the solution smells very faintly of hydrogen sulphide, filter off the yellow precipitate of arsenious sulphide on a Gooch crucible or on a counterpoised filter,* wash with water, then with alcohol, then with pure carbon disulphide, dry at 100° C., and weigh as arsenious sulphide, which contains 60.92 per cent. of arsenic.

FIG. 86



Or, after filtering the precipitate on the felt in a Gooch crucible, transfer the precipitate and felt to a small beaker, add a little fuming nitric acid, and, when action has nearly ceased, heat gently until the sulphur is dissolved, dilute, filter, and evaporate to about 10 c.c. Add 5 c.c. of mag-

* See page 25.

nesia-mixture and then ammonia equal to one-half the volume of the solution. Stir the solution vigorously from time to time, keeping it cool by immersing the beaker in ice-water, and allow it to stand twelve hours. Filter on a Gooch crucible, wash the precipitate of ammonium-magnesium arsenate with the ammonia-water containing ammonium nitrate, used for washing the ammonium-magnesium phosphate (page 80), dry at 103° C. for half an hour, then increase the heat very gradually to redness, and ignite strongly for a few minutes. Weigh as magnesium arsenate, which contains 48.27 per cent. of arsenic.

DETERMINATION OF TIN.

Tin is a most unusual constituent of steel or iron, but has been found in the former in cases where scrap from tinned iron, from which the tin has been removed by a chemical process, has been melted in the open-hearth furnace as a portion of the charge. Dissolve 10 grammes of the sample in hydrochloric acid, and dilute 600 c.c., and saturate the solution with hydrogen sulphide. Allow it to stand for several hours, filter, and wash with water containing hydrogen sulphide. Treat the precipitate on the filter with ammonium sulphydrate, allowing the solution and washings to run into a 250 c.c. beaker. Acidulate with acetic acid, allow to stand in a warm place for several hours, filter, and wash with water containing ammonium acetate made slightly acid with acetic acid. Dry the precipitate and filter, transfer the precipitate to a weighed porcelain crucible, burn the filter and add its ash to the precipitate, add a little sulphur, and ignite in a current of hydrogen sulphide, as directed for the determination of manganese as sulphide (page 107). Any arsenic present will be volatilized, but it is not possible to weigh the tin as sulphide, as its composition is not constant. Heat the crucible carefully, and roast the precipitate with access of air, heat it strongly two or three times with ammonium carbonate to volatilize any sulphuric acid that may have been formed, cool, and weigh as stannic oxide, which contains 78.77 per cent. of tin.

METHODS FOR THE ANALYSIS

OF

ALLOY STEELS

DETERMINATION OF TUNGSTEN.

Besides chromium and tungsten, these steels may contain nickel, vanadium, and molybdenum, as well as the ordinary elements, manganese, silicon, sulphur, phosphorus, and carbon.

When a tungsten or chrome-tungsten steel is dissolved in nitric acid the tungstic acid invariably carries down appreciable amounts of chromium, if present, and iron but by dissolving 2 grammes in 50 c.c. of hydrochloric acid (1 part water to 1 part strong hydrochloric acid) and when solution is complete adding enough nitric acid to oxidize the iron, the tungstic acid is bright yellow in color and contains no chromium and only traces of iron and silica. Dilute with twice the volume of water, boil, cool and filter using double filters and wash with a mixture of 1 part hydrochloric acid to 6 of water. To the filtrate add about .2 gramme of quinine hydrochloride, heat to boiling, boil about 1 minute and cool the solution. This will precipitate any trace of tungstic acid. Filter on double filters and wash with 1 to 6 hydrochloric acid and water containing 1 gramme of quinine hydrochloride to the litre. Dissolve any precipitate of tungstic acid that may have adhered to the beaker in a little ammonia, wash it into a crucible and evaporate to dryness. Place the filters containing the precipitated tungstic acid in the crucible and ignite them. Cool the crucible and pour on the precipitate a few drops of water, 2 drops of sulphuric acid, a little nitric acid and 4 or 5 c.c. pure hydrofluoric acid. Evaporate to dryness at a low heat and ignite carefully. Weigh the crucible, add 1 to 2 grammes sodium carbonate and fuse. Dissolve the fusion in hot water, filter through a small ashless filter and wash thoroughly. Place the filter with the small precipitate of ferric oxide in

the crucible, ignite and weigh. This weight subtracted from the first weight is tungstic acid which contains 79.31 per cent. tungsten. Should the tungstic contain any chromium it will show by a yellow color in the last filtrate. The amount may be estimated by color as directed on page 186, and the amount calculated as Cr_2O_3 subtracted from the weight of the WO_3 before calculating the tungsten. Tungstic acid is not satisfactorily precipitated by quinine except in the strength of acid as noted above.

When determining nickel, chromium and manganese in chrome or chrome-tungsten steels, evaporate the solution from the ether separation nearly to dryness and replace the hydrochloric acid by nitric acid, transfer to a platinum crucible, evaporate to dryness and heat to redness. Fuse with sodium carbonate and a little potassium nitrate. Dissolve the fused mass in hot water, add a little alcohol which will precipitate all the manganese as oxide and allow the precipitate to settle. Wash several times by decantation, adding a little sodium carbonate to the wash water to keep the precipitate from going through the filter. Dissolve the precipitate that adheres to the crucible in hydrochloric acid, pour it on the precipitate in the beaker, ignite the filter, add it to the solution in the beaker and heat until the solution is complete. Dilute to about 100 c.c. with hot water and precipitate by hydrogen sulphide to get rid of the platinum and copper. Boil the filtrate, add bromine to oxidize the iron and precipitate several times by sodium carbonate and sodium acetate. Acidulate strongly with acetic acid and precipitate the nickel by hydrogen sulphide. Filter and determine the nickel by electrolysis. The filtrate from the nickel sulphide contains the manganese. Determine the manganese as directed on page 105.

The filtrate from the fusion obtained above contains the chromium as sodium chromate. Heat to boiling, acidulate with nitric acid, add a little sulphurous acid to reduce the chromic acid and boil off the carbonic acid and excess of sulphurous acid. Precipitate the oxide of chrome with ammonia, boil and filter, wash and ignite the precipitate.

Fuse 5 grammes of sodium carbonate in a small crucible, and when perfectly liquid run it up on the sides of the crucible, so that, when

cold, it will form a lining rather thicker on the bottom than on the sides. Transfer the ignited precipitate of oxide of chrome to the prepared crucible by mixing it with about 1 to 2 grammes of sodium peroxide and heat the prepared crucible until the sodium peroxide is fused. It fuses very easily and quietly, and never spatters. Cool the crucible and place it carefully in a 400 c.c. beaker containing about 100 c.c. of cold water. When the effervescence is over, remove the crucible, wash it thoroughly and heat the contents of the beaker, filter into a 600 c.c. beaker and boil until all the oxygen is driven off, cool, add an excess of sulphuric acid, boil thoroughly, cool and add an excess of a standard solution of ferrous sulphate and titrate the excess of iron with permanganate, as directed on page 186.

DETERMINATION OF VANADIUM.

In the absence of chromium, the method of Campagne is simple and accurate. (Comptes-Rendus, 1903, vol. cxxxvii. p. 570.)

Treat from 1 to 5 grammes by the ether method as described on page 179.* The aqueous solution contains vanadium, chromium, aluminum, manganese, copper, nickel, and cobalt, with a little iron. Evaporate this solution several times with a large excess of hydrochloric acid and reduce the vanadic acid to di-vanadyl chloride, according to the equation, $V_2O_5+6HCl=2VOCl_2+3H_2O+Cl_2$. Add 5 c.c. of strong sulphuric acid and evaporate until all the hydrochloric acid is expelled and fumes of sulphuric acid appear. By this operation di-vanadyl sulphate is formed:

$$2VOCl_2+2H_2SO=V_2O_2(SO_4)_2+4HCl.$$

Allow it to cool and dilute to 200 or 300 c.c. Warm to about 60° C. and titrate with permanganate solution.

$5V_2O_2(SO_4)_2 + 2KMnO_4 + 8H_2SO_4 = 5V_2O_2(SO_4)_3 + K_2SO_4 + 2MnSO_4+8H_2O$. Now, as $10FeSO_4+2KMnO_4+8H_2SO_4=5Fe_2(SO_4)_3+K_2SO_4+2MnSO_4+8H_2O$, then $10V = 510$ is equal to $10Fe = 558.4$, or

$$\text{Vanadium} = .9133\ \text{Fe}.$$

The vanadium equals the value of the permanganate solution in iron multiplied by .9133.

* Do not evaporate the solution to dryness as the chloride of vanadium is slightly volatile.

Small amounts of ferric salts do not interfere with the reaction, but when chromium is present to the extent of 2 per cent. or over, the color of the chrome salt masks the end reaction. The color of the di-vanadyl sulphate is pale blue, while that of the chromium sulphate is green. It is, therefore, impossible to tell from the color of the solution under the conditions whether the sample contains vanadium or not, the discoloration of the permanganate solution being the only indication of its presence.

Cain's Method.

A very interesting and acurate method for the determination of vanadium in steel has been worked out by Mr. J. R. Cain, of the Bureau of Standards.*

It is based on the fact that in a reduced iron solution containing a small amount of ferric salt the vanadium is entirely precipitated with the ferric oxide by an excess of barium or cadmium carbonate, the iron and chromium being finally separated from the vanadium by electrolysis with a mercury cathode.

The details of the method are as follows:—

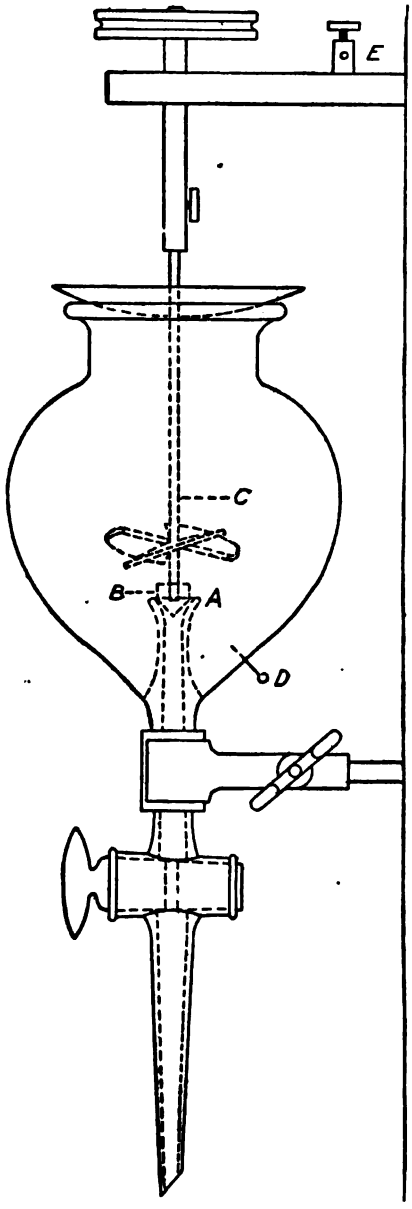
Dissolve from 2 to 5 grammes of the sample in a 300 or 500 c.c. Erlenmeyer flask in 40 to 100 c.c. of 10 per cent. (by volume) sulphuric acid. Filter into a similar flask, ignite and fuse the insoluble matter with a small amount of acid potassium sulphate, dissolve the melt in water and add it to the solution in the flask. Nearly neutralize the solution with sodium carbonate, heat it to boiling and add cadmium carbonate in an emulsion until the effervescence ceases and there remains an appreciable amount of cadmium carbonate undecomposed in the solution, which shows as a white precipitate on the bottom of the flask. Boil vigorously for 10 to 15 minutes, keeping the flask covered to prevent unnecessary oxidation of the iron. Allow the precipitate to settle, filter as rapidly as possible and wash several times with hot water.

Dissolve the precipitate on the filter with a minimum of nearly boiling 10 per cent. sulphuric acid, allowing the solution and wash

* *Journal of Industrial and Engineering Chemistry*, vol. 3, p. 476.

water to run into the flask in which the precipitation was made, and boil to ensure the solution of any precipitate adhering to the sides of the flask. Dilute to about 200 c.c. and pass a rapid current of hydrogen sulphide through the boiling solution to precipitate the cadmium. Filter, wash several times with hot water and concentrate the solution to about 60 or 70 c.c. Nearly neutralize the solution with ammonia and electrolyze with a current of 5 to 6 amperes and about 5 volts, using a mercury cathode. The apparatus suggested by Mr. Cain (Fig. 87) is admirable for the purpose. It consists of a separatory funnel, with the exit tube A projecting into the bulb and slightly expanded at the end to allow the hard rubber cone B to fit into it. The cone into which the platinum anode C is screwed insulates the anode and holds it in place while it rotates freely in the solution. The anode is formed of a platinum rod passing through a disc of platinum cut through in three places with the edges turned down to form a propeller which stirs the liquid thoroughly. The upper end of the anode passes through a perforated watch-glass to prevent loss by the spattering of the solution and is attached to the pulley by a brass sleeve. One wire of the battery is attached to the support at E and the other is hooked

FIG. 87.



into the platinum wire which is fused to the bulb, as shown at D. Mercury is poured into the bulb, filling it almost to the top of the tube A, which is also filled with mercury above the stop-cock. The bulb should have a capacity of about 125 c.c. With a properly neutralized solution and current of the strength noted, all the iron and chromium should be deposited in the mercury in about 30 minutes.

When the electrolysis is completed, open the stop-cock and while the current is still passing allow the liquid to run into a beaker while the watch glass and the sides of the bulb are washed with a jet of water from a wash-bottle. Filter from the mercury, etc., add about 5 c.c. of strong sulphuric acid, heat to boiling and add permanganate until the liquid has a bright pink color. Pass a current of sulphur dioxide into the boiling solution for several minutes and then carbon dioxide until every trace of sulphur dioxide is expelled. Cool to 70° or 80° C. and titrate with potassium permanganate as on page 198.

DETERMINATION OF SULPHUR

It is of course necessary to dissolve these steels in strong nitric acid to avoid loss of sulphur and as solution is difficult it is usually necessary to boil them for some hours before decomposition is complete. After this the procedure is the same as in ordinary steels except in chrome steels. The presence of much chromium prevents the neutralization by evaporation, by the tendency of the chromic chloride to separate out and become insoluble before the ferric chloride begins to separate. It is necessary therefore to neutralize the solution after filtering off the silica and tungstic acid as directed on page 63.

If the precipitated barium sulphate is not perfectly white and granular it may be contaminated by a little tungstic acid which may be removed by washing with a little dilute ammonia after washing the filter free from iron with dilute hydrochloric acid and water.

DETERMINATION OF PHOSPHORUS

Decompose 2 grammes of the sample with nitric acid and water 1 to 3, add hydrochloric acid and evaporate to dryness. Redissolve in hydrochloric acid, dilute, boil and filter off the tungstic acid. Evaporate the

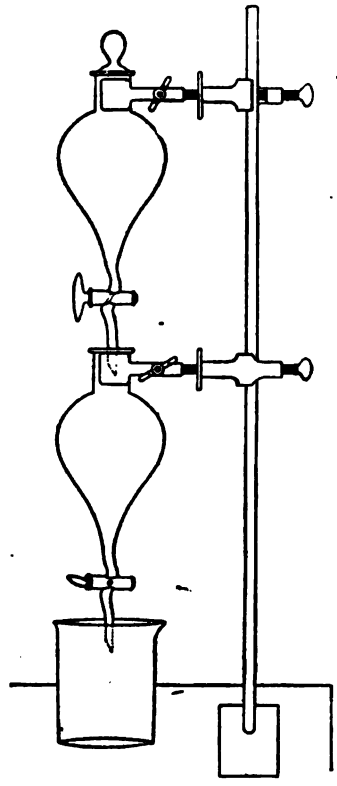
filtrate to small bulk, add nitric acid, boil down, add nitric acid a second time to get rid of the hydrochloric acid, transfer to a flask and precipitate the phosphorus by molybdate solution as directed on page 93.

DETERMINATION OF SILICON, TUNGSTEN, VANADIUM, MOLYBDENUM, CHROMIUM AND MANGANESE.

Dissolve two grammes of the sample in 60 c.c. of hydrochloric acid 1.1 sp. gr., and when the action has ceased add about 5 c.c. of nitric acid and boil for a few minutes to thoroughly oxidize it. Dilute to about 150 c.c. with hot water and boil again. Cool, filter on a double filter, wash with hydrochloric acid and water 1 to 6. Ignite the precipitate of tungstic acid and silica in a crucible and put it aside. Evaporate the filtrate to dryness but do not heat above 100°, as the vanadium is volatile at high temperatures. Add a little hydrochloric acid and evaporate a second time. Dissolve in hydrochloric acid 1.1 sp. gr., dilute slightly and filter off the silica which add to the tungstic acid in the crucible; ignite and weigh. Add 2 to 3 drops of sulphuric acid and 5 to 10 c.c. hydrofluoric acid, evaporate to dryness, ignite and weigh. The loss is silica, which contains 46.93 per cent. silicon. Treat the residue for tungsten as directed on page 196. The filtrate from the silica is almost always absolutely free from tungstic acid. Evaporate this solution to syrupy consistency, add a little hydrochloric acid 1.1 sp. gr, and cool in ice water. Add 2 to 5 drops of sulphurous acid to the solution to reduce the vanadium to the vanadyl condition, and wash it into a separatory funnel of about 250 c.c. capacity, using a minimum amount of hydrochloric acid 1.1 sp. gr. cooled in ice water. The separatory funnel should be of the form shown in Fig. 88 fitted at the lower end with a Geissler stop-cock and at the upper end with a glass stopper both carefully ground to prevent leakage. Add to the solution in the funnel about 80 c.c. of ordinary ether and shake vigorously for half a minute. An ordinary clamp with cork-lined jaws supported on a stand makes a convenient arrangement for holding the funnel. When the two strata have separated, open the stop-cock and allow the lower to run into

another separatory funnel as shown in Fig. 88.* Remove the stopper, wash the solution down with about 10 or 15 c.c. of hydrochloric acid 1.1 sp. gr., shake again and allow the washings to run into the other funnel. Add 50 c.c. of ether to the solution in the second funnel to remove as much of the remaining iron as possible, run the acid solution into a beaker and evaporate nearly to dryness. Add nitric acid in excess and evaporate until all the hydrochloric is expelled and finally, when the solution is almost syrupy, add 20 c.c. of hot water. Heat the solution and add a few drops of sulphurous acid to reduce any chromic acid that may have been formed. Boil and pour the solution drop by drop, stirring vigorously, into 100 c.c. of a boiling solution of sodium hydroxide containing 100 grammes sodium hydroxide to the litre. Boil the solution for a few minutes, allow the precipitate to settle, filter, wash twice by decantation and finally on the filter until the filtrate measures about 300 c.c. in volume. The precipitate consists of the oxides of chromium, nickel, and iron, with the greater part of the manganese and any copper that may have been in the sample. The filtrate contains the vanadium, some silica and alumina from the sodium hydroxide, and sometimes a little chromium. Add dilute nitric acid to the filtrate until it just turns blue litmus paper red, then add a few drops of sodium hydroxide solution to make it alkaline, boil and filter. To the filtrate add enough acetic acid to make it decidedly acid to litmus paper and boil for several minutes, then add

FIG. 88.



* The second funnel may be dispensed with and the solution or washings run directly into the beaker as the small amount of iron in the solution is usually of no importance.

10 c.c. of a 10 per cent. solution of lead nitrate and boil. Filter the precipitate, which contains all the vanadium as lead vanadate, and wash with hot water. Dissolve in hot dilute hydrochloric acid, allow to run into a 400 c.c. beaker, add 5 c.c. strong sulphuric acid and evaporate until the sulphuric acid fumes freely. Cool, dilute slightly, add permanganate solution and boil to destroy organic matter. Evaporate twice with 25 c.c. of hydrochloric acid to reduce the vanadium to the vanadyl condition, then evaporate until the sulphuric acid fumes, cool, dilute to 150 c.c. and titrate at a temperature of 60° to 70° with permanganate as on page 198. The presence of small amounts of iron does not affect the accuracy of the method and the trouble of boiling off every trace of sulphurous acid when this reagent is used, is avoided.

The two precipitates obtained from the sodium hydroxide solution contain chromium, nickel, and copper, besides iron and manganese. Ignite the two filters and precipitates and fuse in a crucible lined with sodium carbonate with 2 grammes of sodium peroxide. (As on page 185.) Treat the fused mass with water, boil and filter. The insoluble portion contains the nickel, copper, iron, and manganese, and the filtrate, the chromium. To the filtrate add dilute-sulphuric acid and titrate as on page 185.

Return the filter, containing the insoluble matter from the fusion, to the crucible in which the fusion was made, ignite, dissolve in hydrochloric acid, dilute and precipitate the iron twice with sodium acetate as directed on page 103. Precipitate the nickel by hydrogen sulphide and determine the amount by electrolysis. The filtrate from the nickel contains manganese which may be precipitated by bromine as directed on page 105. Filter and dissolve this precipitate in sulphurous acid with a little nitric acid and determine the manganese by the bismuthate method. As the separation of nickel and manganese is troublesome, it is better to determine the nickel in a separate portion by the dimethylglyoxime method page 184, and the manganese in the insoluble matter from the fusion in sodium peroxide. Dissolve this precipitate in the filter in sulphurous acid with the addition of nitric acid allowing the solution to run into an Erlenmeyer flask. Clean out the crucible with the same solvent. Use a measured volume of nitric acid, say 20 c.c., and let the total volume

of the solution and washings in the flask be about 80 c.c. Boil until the nitrous fumes are driven off, cool and determine the manganese by the bismuthate method.

To the ethereal solution of the iron which remains in the two separatory funnels, add water and shake. Draw off the ferric chloride containing the molybdenum which separates from the ether and evaporate nearly to dryness, add 10 c.c. strong sulphuric acid and evaporate carefully until the hydrochloric acid is driven off and the sulphuric acid fumes freely. Cool, dissolve in about 100 c.c. water and carefully deoxidize with ammonium bisulphite, boil off the excess of sulphurous acid and cool the solution. Transfer the cold solution to a pressure bottle of 200 c.c. capacity and pass a current of hydrogen sulphide through it until it is saturated, close the bottle and heat it on a water-bath for several hours. Allow it to cool slowly. Filter on a Gooch crucible, wash the precipitate first with water containing a little sulphuric acid and finally with alcohol. Place the Gooch crucible containing the precipitate on a small triangle placed inside a large porcelain crucible so that the bottom of the Gooch crucible shall not touch the porcelain crucible. Cover the latter with a watch glass and heat it carefully, raising the heat gradually until there is no smell of sulphurous acid. Replace the watch glass with a porcelain cover and heat until the precipitate of molybdenum sulphide becomes bluish-white in color.

Place the Gooch crucible over a lamp and heat it to faint redness, cool and weigh. Heat it again to faint redness, weigh, and repeat the operation until it ceases to lose weight. Place the crucible on the vacuum flask and dissolve the molybdic trioxide in dilute ammonia, wash, heat and weigh the crucible. The difference between the two weights is molybdenum trioxide, which contains 66.67 per cent. molybdenum. There always remains on the felt in the Gooch crucible a small amount of oxide of iron.

It is necessary to precipitate the molybdenum sulphide from a sulphuric acid solution as it is almost impossible to separate all the molybdenum sulphide in one operation from a hydrochloric acid solution.

The interesting fact that the molybdenum is found in the ethereal solution

seems to be due to the presence of the large amount of ferric chloride; for in a number of experiments I made bearing on this point, in the absence of ferric chloride a solution of molybdenum trioxide in hydrochloric acid was found partly in the ether and partly in the acid solution. I have not had time to determine the relative amount of molybdenum that will go with the ethereal ferric chloride, but for any amount that may be used as an alloy in steel the separation may be regarded as strictly quantitative.

The nitric acid solution of the vanadium, chromium, and nickel must be poured slowly into the boiling sodium hydroxide solution; for if the operation is reversed and the chromium and nickel are simply precipitated by sodium hydroxide the greater part of the vanadium will be carried down with the precipitated oxides.

The addition of a few drops of sulphurous acid to the nitric acid solution, page 203, is very necessary as a little chromium is always present as chromic acid. This is shown by the change in the solution, which loses its slightly brownish tint and becomes light blue in color.

DETERMINATION OF CARBON

Carbon is determined by direct combustion in a current of oxygen.

ANALYSIS OF COBALT STEEL

The so-called cobalt steel is usually a tungsten, chrome, vanadium, molybdenum steel with several per cent. of cobalt added to give special characteristics to the material. The presence of cobalt in the amount usually found in these steels prevents the precipitation of nickel by di-methylglyoxime in the usual way.

DETERMINATION OF COBALT.

Dissolve 1 to 2 grammes of the drillings in a 250 c.c. beaker in 40 c.c. of hydrochloric acid 1.1 sp. gr. oxidize with nitric acid and evaporate to dryness. Redissolve in 20 c.c. strong hydrochloric acid and evaporate to syrupy consistency. Make an ether separation as directed on page 178 or 202.

(If tungsten is present it must be filtered off before evaporating to dryness.)

Heat the solution in the beaker containing the nickel, cobalt, etc., to drive off the ether and evaporate to about 10 c.c., add 25 c.c. of cold water and a freshly prepared solution of 10 to 20 grammes of potassium nitrite dissolved in a little water and made faintly acid with acetic acid and treat as on page 175.

After filtering and washing the precipitate dissolve it in 20 c.c. sulphuric acid and water 1 to 2, allowing the solution to run into the beaker in which the precipitation was made, wash with hot water, evaporate the solution until fumes of sulphuric acid are given off and precipitate the cobalt by electrolysis.

DETERMINATION OF NICKEL.

Acidulate the filtrate from the potassium cobalt nitrite with sulphuric acid and evaporate until fumes of sulphuric acid are given off.

Dilute with water to about 300 c.c., add 5 to 10 grammes of citric acid and a slight excess of ammonia, cool and precipitate by dimethylglyoxime and determine the nickel as described on page 182.

DETERMINATION OF SILICON, TUNGSTEN, CHROMIUM, VANADIUM AND MANGANESE.

Treat 2 grammes of the steel exactly as described on page 202, until the nitric acid solution has been dropped into the solution of sodium hydroxide and the two precipitates containing the nickel, cobalt and manganese are ignited and dissolved in hydrochloric acid. (The chromium and vanadium are determined in the filtrate from these precipitates and the molybdenum in the ethereal solution of the iron.) Evaporate this solution to syrupy consistency, add 10 drops of hydrochloric acid and 20 c.c. of cold water. Precipitate the cobalt by potassium nitrite as described on page 175. The filtrate and washings from the precipitate of potassium cobalt nitrite contains the manganese, nickel and the small amount of iron which was not separated by the ether.

Heat the solution to boiling and precipitate by a slight excess of potassium hydroxide. Filter and wash with hot water. Dissolve the precipitate in a little hot dilute sulphuric acid containing a few drops of sulphurous acid and evaporate until the sulphuric acid fumes freely, to get rid of the last trace of hydrochloric acid which may have remained in the precipitate by potassium hydroxide. Treat the sulphuric acid solution with nitric acid and water 1 to 3 and transfer it to a flask, using 60 c.c. of the dilute acid and determine the manganese by the bismuthate method, page 116. It is necessary to separate the manganese from the cobalt in using the bismuthate method, as the cobalt is oxidized by the bismuthate and the results are vitiated by the presence of cobalt in the solution.

ANALYSIS OF URANIUM STEEL

DETERMINATION OF URANIUM.

Boil 2 grammes of the drillings with 50 c.c., 1–1 hydrochloric acid and water until decomposition is complete, and treat as in the analysis of Chrome Tungsten steels until the separation by ether has been made. The acid solution contains the uranium as well as the chromium, venadium, etc. Boil off the ether, evaporate to dryness, redissolve in hydrochloric acid, filter off the silica and precipitate by ammonia. Filter and wash the precipitate of uranium, chromium, etc. Dry and ignite the precipitate and fuse it in a crucible lined with sodium carbonate with an excess of sodium peroxide. Place the cold crucible on its side in a 350 c.c. beaker and add a small amount of cold water. When the violent action has ceased, add hot water, and finally remove the crucible and wash all the material into the beaker. Boil 15 minutes to decompose all the sodium peroxide. The chromium will all be in solution as chromate while the oxides of iron, manganese, nickel and cobalt will be insoluble and the uranium partly in solution and partly insoluble. If the steel is a so-called "Cobalt Steel" the voluminous black insoluble matter will be largely oxide of cobalt and the procedure in this event will be indicated further on. If not, acidulate the solution with dilute sulphuric acid and boil off all the carbonic acid. Add an excess of ammonia, boil, filter and wash with water containing a little ammonia. The filtrate may be used for the determination of chromium. Dissolve the precipitate in dilute nitric acid containing a few drops of sulphurous acid to dissolve any manganese oxide that may be present, allowing the filtrate and washing to run into a small beaker. Evaporate to dryness but do not heat above 100° C. Dissolve in a few drops of nitric acid, dilute to 25 c.c. with cold water, add a slight excess of ammonia and then 1 to 2 grammes of ammonium carbonate and digest at a temperature of 40° to 50° C. with constant stirring for 15 or 20 minutes. Filter wash with water containing 3 or 4 grammes of ammonium carbonate to the litre. Boil the filtrate which contains all the uranium in solution in the ammonium carbonate until the carbonate is driven

off. If uranium is present it will be precipitated as a whitish yellow oxide as soon as the ammonium carbonate is driven off. Add just enough nitric acid to dissolve the precipitate, boil, and allow the solution to cool. Add to the solution 10 c.c. of a solution of sodium vanadate, made by treating 1 gramme of vanadic acid in just enough sodium carbonate solution to dissolve it and diluting to 112 c.c., 1 c.c. of which will contain .005 gramme vanadium. Now add dilute ammonia to the solution, which should measure about 150 c.c. in volume, until a distinct permanent precipitate is formed and just dissolve this by adding dilute nitric acid drop by drop. Add 10 to 15 c.c. ammonium acetate, made by adding 30 per cent. acid to strong ammonia, until the solution is just acid to litmus paper. This will require a little over three volumes of acetic acid to one of ammonia. Boil vigorously for 10 to 15 minutes and remove from the source of heat. The precipitate which settles readily is the canary yellow ammonium uranyl vanadate $V_2O_5 2UO_3 (NH_4)_2 + H_2O$ mentioned by Carnot.

Decant the clear liquid on a filter, pour on the precipitate, and wash two or three times with hot water containing 5 c.c. of the ammonium acetate mentioned above to 100 c.c. water. Dissolve the precipitate adhering to the beaker in a little dilute nitric acid and pour it on the filter, allowing the solution to run into a 250 c.c. beaker. Wash the filter with a little hot dilute nitric acid and then with hot water and evaporate the solution to dryness, but do not heat above 103° C. Dissolve in a little very dilute hot nitric acid, add ammonia until a precipitate forms, and then add to the solution, the temperature of which should not be above 40° C., 1 to 2 grammes ammonium carbonate. This will dissolve the uranium and vanadium and precipitate any silica and alumina present. Digest for a few minutes with constant stirring, filter and wash with ammonium carbonate solution. Boil to expel the excess of ammonium carbonate, acidulate with nitric acid, cool, and boil to drive off the carbonic acid, cool, and precipitate as directed above with ammonium acetate in the faintly acid solution. Filter, wash, ignite at a low red heat and weigh as $V_2O_5 2UO_3$, which contains 63.15 per cent. uranium ($V = 51.0$ $U = 238.2$).

In the case of cobalt steels referred to above it is better, after boiling to decompose the sodium peroxide, to cool the solution and saturate it with carbon dioxide or add an excess of sodium bicarbonate. Uranium salts are soluble in the carbonates of the alkalies but insoluble in an excess of alkaline hydroxide, and it is therefore necessary to convert the hydroxide into

carbonate to get the uranium all in solution. Filter and wash the insoluble matter, which consists principally of oxide of cobalt, with whatever oxides of iron and manganese may have been present with water containing a little sodium carbonate. The filtrate contains the chromic acid and uranium oxide. Acidulate the filtrate with dilute sulphuric acid and boil off all the carbonic acid. Add an excess of ammonia, which will precipitate the uranium, boil and wash with hot water containing a few drops of ammonia. Dissolve the precipitate in a little hot dilute nitric acid and wash the filter with hot water, receiving the solution and washings in a small beaker. Add 10 c.c. of the sodium vanadate, neutralize and precipitate by ammonium acetate, boil 10 to 15 minutes, filter and wash with water containing ammonium acetate. Dissolve in nitric acid, evaporate to dryness, take up with a little nitric acid, treat with ammonia and ammonium carbonate, filter and reprecipitate as above. Filter, wash, ignite and weigh as $V_2O_5 2UO_3$. It would be possible to weigh the uranium as U_3O_8 except that these steels all seem to contain vanadium and this always precipitates with the uranium, and it is better to add an excess of vanadium and determine the uranium as above described.

DETERMINATION OF OXYGEN IN STEEL AND IRON.

A method for the determination of oxide in steel and iron is given on page 74, but sometimes a direct determination of oxygen is desired and for this the method suggested by Ledebur is generally used. This consists essentially in heating the sample in a current of hydrogen and collecting and weighing the water produced. The apparatus, Fig. 54, with a few changes answers perfectly for this method. Quartz tubes are used which are closed with perforated rubber stoppers fitted with short lengths of ¼-inch glass tubes and the connections are made with pure gum tubing, the ends of all the glass tubes and connected U tubes being in close contact.

Instead of the oxygen tank a Kipp generator or an arrangement like that shown in Fig. 44 for generating hydrogen gas is used. The hydrogen should be generated from zinc, as pure as it can be obtained, and hydrochloric acid and water 1 to 1. The hydrogen passes first through a tube L, Fig. 56, containing sodium hydroxide 1.27 sp. gr. and then through a tube N containing sodium hydroxide in sticks or lumps. From this it passes through a platinum or quartz tube containing spongy platinum or platinized asbestos to insure the removal of any oxygen which may be with the hydrogen. The

gas then passes through a U-tube containing granulated calcium chloride dried at 270° C. From this the gas passes through a ¾-inch quartz tube containing the sample in a platinum or quartz boat and then through a weighed U-tube containing calcium chloride of the same quality and then through a guard tube of the same character. The sample should consist of fine shavings, turnings or drillings free from all traces of dirt and grease. If drillings are used for the sample, drilling should be done very slowly to avoid heating and surface oxidation.

Connect the apparatus without the boat in the tube and without the absorption U-tube of calcium chloride and heat the large quartz tube while passing a stream of air through it to destroy any dust or carbonaceous matter and allow it to cool. When cold turn off the air, insert the boat containing 10 to 20 grammes of the sample, attach the weighed calcium chloride U-tube with its guard tube, start a current of hydrogen through the apparatus and when certain that the air is all expelled, light the burners under the preheater tube. When the purified hydrogen fills the large tube, heat the latter gradually to the full extent of the furnace and allow it to run for 30 minutes while passing the gas at the rate of 5 or 6 bubbles a second. Turn off the heat under the large tube and allow the hydrogen to run until the tube is cool to the hand, then stop the hydrogen and replace it in the tubes with air. Detach and weigh the absorption tube of calcium chloride. Several blanks should be made to determine the amount to be subtracted from the increase in weight of the calcium chloride tube. Eight-ninths of the net increase is oxygen. The calcium chloride tube should be closed when removed from the apparatus with the arrangement described on page 132. The blank should not exceed 1 to 2 milligrammes.

There is a great difference of opinion among analysts as to the merits of the different drying agents, fused calcium chloride, dried calcium chloride, concentrated sulphuric acid, and phosphorous pentoxide. It is safe to say, however, that in a method like this the same drying agent should be used for the gas when leaving the tube as when entering it. In an article "Granular Calcium Chloride as a Drying Agent" (*Jour. Amer. Chem. Soc. Col.* xxxix, page 1317) A. T. McPherson shows that granular calcium chloride dried at 270° C. is as efficient as phosphorus pentoxide. It may be dried in the U-tube; it can be used almost indefinitely and is much more convenient than any of the others. It should be dried or changed frequently.

DETERMINATION OF NITROGEN.

This method is based on the reaction by which the nitrogen in iron and steel is converted into ammonia by hydrochloric acid during the solution of the steel in this reagent.

It was first published by A. H. Allen,* with many interesting details and results. The modifications of the method as described by Mr. Allen are by Prof. J. W. Langley,† of Pittsburgh, and consist in the use of caustic soda freed from nitrates and nitrites by the copper-zinc couple and subsequent distillation of all ammonia formed, and in a few details of manipulation.

The reagents required are:

Hydrochloric acid of 1.1 sp. gr., free from Ammonia, which may be prepared by distilling pure hydrochloric acid gas into distilled water free from ammonia. To do this, take a large flask fitted with a rubber stopper carrying a separatory funnel-tube and an evolution-tube, fill it half full of strong hydrochloric acid, connect the evolution-tube with a wash-bottle connected with a bottle containing the distilled water. Admit strong sulphuric acid free from nitrous acid to the flask through the funnel-tube, apply heat as required, and distil the gas into the prepared water.

Test the acid by admitting some of it into the distilling apparatus, described farther on, and distilling it from an excess of pure caustic soda, or determine the amount of ammonia in a portion of hydrochloric acid of 1.1 sp. gr., and use the amount found as a correction.

Solution of Caustic Soda, made by dissolving 300 grammes of fused caustic soda in 500 c.c. of water, and digesting it for twenty-four hours at 50° C. on a copper-zinc couple, made, as described by Gladstone & Tribe, as follows: Place from 25 to 30 grammes of thin sheet zinc in a flask and cover with a moderately concentrated, slightly warm solution of copper sulphate. A thick spongy coating of copper will be deposited on the zinc. Pour off the solution in about ten minutes and wash thoroughly with cold distilled water.

Nessler Reagent. Dissolve 35 grammes of potassium iodide in a small quantity of distilled water, and add a strong solution of mercuric chloride little by little, shaking after each addition, until the red precipitate formed dissolves. Finally the precipitate formed will fail to dissolve, then stop the addition of the mercury salt and filter. Add to the filtrate 120 grammes of

* Chemical News, xli. 231. † Communicated to the author.

caustic soda dissolved in a small amount of water, and dilute until the entire solution measures 1 litre. Add to this 5 c.c. of saturated aqueous solution of mercuric chloride, mix thoroughly, allow the precipitate formed to settle, and decant or siphon off the clear liquid into a glass-stoppered bottle.

Standard Ammonia Solution. Dissolve 0.0382 gramme of ammonium chloride in 1 litre of water; 1 c.c. of this solution will equal 0.01 milligramme of nitrogen.

Distilled Water free from Ammonia. If the ordinary distilled water contains ammonia, redistil it, reject the first portions coming over, and use the subsequent portions, which will be found free from ammonia. Several glass cylinders of colorless glass of about 160 c.c. capacity are also required.

The best form of distilling apparatus consists of an Erlenmeyer flask of about 1500 c.c. capacity, with a rubber stopper, carrying a separatory funnel-tube and an evolution-tube, the latter connected with a condensing-tube around which passes a constant stream of cold water. The inside tube, where it issues from the condenser, should be sufficiently high to dip into one of the glass cylinders placed on the working-table.

The determination of nitrogen is made as follows. Place 30 c.c. of the caustic soda, which has been treated with the copper-zinc couple, in the Erlenmeyer flask, add 500 c.c. of water, and distil until the distillate gives no reaction with the Nessler reagent. While this part of the operation is in progress, dissolve 3 grammes of the carefully washed drillings in 30 c.c. of the prepared hydrochloric acid, using heat if necessary. Transfer the solution to the bulb of the separatory funnel-tube, and when the soda solution is free from ammonia, drop the ferrous chloride solution into the boiling solution in the flask, very slowly. The ferrous hydrate formed is apt to stick to the bottom and sides of the flask and cause it to break. When about 50 c.c. of water have been collected in the cylinder, remove it and substitute another cylinder. Place 1½ c.c. of the Nessler reagent in a cylinder, dilute the distillate to 100 c.c. with the special distilled water and pour it into the cylinder containing the Nessler reagent. Take another cylinder, place 1½ c.c. of the Nessler reagent in it, and pour into it 100 c.c. of the special distilled water to which 1 c.c. of the ammonium chloride solution has been added, and compare the colors of the solutions in the two cylinders. If the solution in the cylinder containing the ammonium chloride solution is lighter in color than in the cylinder containing the distillate, place 1½ c.c. of the

Nessler reagent in another cylinder, pour into it 100 c.c. of water containing 2 or more c.c. of the ammonium chloride solution, and repeat this operation until the colors of the solutions in the two cylinders correspond after standing about ten minutes. When about 100 c.c. have distilled into the second cylinder, replace it and test as before. Continue the distillation until the water comes over free from ammonia, then add together the number of c.c. of ammonia solution used, divide the sum by 3, and each 0.01 milligramme will be 0.001 per cent. of nitrogen in the steel.

DETERMINATION OF IRON.

The combined carbon in steel and iron interferes with a direct determination of the amount of metallic iron by solution of the drillings in hydrochloric or sulphuric acid and direct titration. It is always necessary to oxidize the iron and carbonaceous matter in the solution, and the process may be carried out as follows:

Dissolve .5 gramme of the drillings in a small flask, as described for the determination of iron in iron ores, in hydrochloric acid, add potassium chlorate in small crystals until the iron is all oxidized and an excess of potassium chlorate is present, boil until all the yellow fumes have disappeared, and then proceed as in the determination of iron in iron ores (page 245). Instead of potassium chlorate, potassium permanganate or chromic acid may be used to oxidize the iron and destroy the carbonaceous matter. In pig-irons the most satisfactory method is to fuse .5 gramme of the borings in a large platinum crucible with 10 grammes sodium carbonate and 2 grammes potassium nitrate, dissolve in hot water, transfer to a small beaker, allow the ferric oxide to settle, decant on a small filter, and wash several times by decantation. After the last decantation, remove the beaker containing the filtrate and place the beaker containing the ferric oxide under the funnel. Dissolve any adhering oxide in the crucible with hydrochloric acid, dilute slightly, and pour it on the filter to dissolve the small amount of oxide, allowing the solution to run into the beaker. Wash the filter if necessary, add more hydrochloric acid to the solution in the beaker, evaporate down, transfer to a small flask, deoxidize, and titrate as before. In the case of puddled iron, it is necessary to subtract the iron in the "slag and oxides" from the total iron obtained as above to get the amount of *metallic iron* in the sample.

METHODS FOR THE ANALYSIS
OF
ALLOY METALS

THE ANALYSIS OF FERRO-TUNGSTEN AND TUNGSTEN METAL.

FERRO-TUNGSTEN.

Determination of Tungsten by Fusion.

Fuse .5 gramme of the finely ground material with 8 grammes of sodium carbonate and 1.5 gramme of potassium nitrate. Dissolve the fused mass in water and boil thoroughly with the addition of a small amount of filter paper pulp, which will precipitate any manganese that may be present. Filter and wash thoroughly with boiling water to which a little sodium carbonate may be added. The use of double filters for this purpose is desirable. Dilute the filtrate to about 500 c.c. and add nitric acid until the solution is faintly but decidedly acid to litmus paper. Boil the solution until the carbon dioxide is driven off and then add 15 c.c. of mercurous nitrate prepared as directed on page 52. The precipitate of mercurous tungstate is pale yellow, almost white in color. Now add mercuric oxide diffused in water (page 52) until the precipitate becomes decidedly reddish-yellow in color. Boil for a few minutes vigorously. There is no tendency to "bump" and when removed from the source of heat the precipitate settles instantly. Decant the supernatant liquid through a filter and wash by decantation four times with boiling water, stirring vigorously each time and then six times on the filter. The precipitate shows no tendency to pass through the filter, but generally as the filtrate cools a yellowish crystalline precipitate shows in it which contains no trace of tungsten. Wipe the adhering precipitate from the rod and beaker with filter paper. Dry the precipitate and filter and transfer the precipitate, which is quite voluminous and heavy, to a

platinum crucible, burn the filter and pieces of filter paper used for wiping the beaker in a coil of platinum wire and add the ashes to the precipitate.

Heat the crucible under a hood with a good draft, raising the heat gradually until the mercury is volatilized and the tungstic acid remains as a lemon-yellow mass. Cool, add a few drops of water, two drops of strong sulphuric acid, a little nitric acid and 3 or 4 c.c. of hydrofluoric acid. Evaporate carefully to avoid spurting, the arrangement shown in Fig. 9 is very useful for this purpose, using an asbestos ring a little larger than the crucible and supporting the latter on a triangle. Finally ignite strongly and weigh. Fuse the precipitate with 1–2 grammes of sodium carbonate, dissolve in water, filter from the small insoluble oxide of iron, wash, burn the filter in the same crucible and weigh. The difference in the weights is WO_3, which contains 79.31 per cent. tungsten. The tungstic acid may contain a little phosphoric acid which in very accurate determinations must be subtracted from the tungstic acid before caculating the tungsten. The phosphoric acid of course is in the solution filtered from the small precipitate of oxide of iron noted above and may be determined as directed for the determination of phosphorus in this material, page 218.

Determination of Tungsten by Solution in Nitric and Hydrofluoric Acids.

Treat .5 gramme of the finely ground material in a platinum dish with 50 c.c. of nitric acid and water 1 to 1. Heat to boiling and add hydrofluoric acid, a few drops at a time, until the material is dissolved. Add 5 c.c. strong sulphuric acid and evaporate until the sulphuric acid fumes freely. Cool, add 25 c.c. hydrochloric acid and water 1 to 1 and boil for 5 to 10 minutes. Add 60 c.c. of hot water, filter through double ashless filters and wash with hydrochloric acid and water 1 to 6. To the filtrate add .1 to .2 gramme quinine hydrochloride, heat to boiling and cool. Filter, wash with hydrochloric acid and water 1 to 6, containing 1 gramme quinine hydrochloride to the litre. Dissolve any tungstic acid that may adhere to the dish and beaker in a little ammonia, wash into a platinum crucible and evaporate to dryness. Place the filters containing the two precipitates of tungstic acid in the crucible, ignite and weigh. Fuse the tungstic acid in 1 to 2 grammes sodium carbonate, dissolve in water, filter, ignite and weigh in the same crucible. The differ-

ence between the two weights is tungstic acid which contains 79.31 per cent. tungsten. The presence of even small amounts of hydrofluoric acid seems to interfere with the complete precipitation of the tungstic acid so that the results obtained by this method may be a little low.

Determination of Sulphur.

Fuse 2 grammes of the finely ground material with 12 grammes sodium carbonate and 5 grammes potassium nitrate, using an alcohol burner. Dissolve in water and filter, preferably into a porcelain beaker or dish, and add an excess of hydrochloric acid. Evaporate to dryness, cool, add 20 c.c. strong hydrochloric acid and evaporate again to dryness. Cool, add 40 c.c. hydrochloric acid and water 1 to 1 and heat to boiling. Add 100 c.c. hot water, boil for a few minutes and filter. Wash with hydrochloric acid and water 1 to 6, and to the filtrate add quinine hydrochloride. Heat to boiling, cool, filter and wash with hydrochloric acid and water 1 to 6 containing 1 gramme of quinine hydrochloride to the litre. Neutralize the filtrate with ammonia, acidulate with 10 drops hydrochloric acid, boil, add barium chloride and boil for a few minutes. Allow to stand over night, filter and wash the precipitate of barium sulphate thoroughly with hot water. Ignite and weigh as barium sulphate, which contains 13.734 per cent. of sulphur. If the precipitate is not perfectly crystalline it may contain tungstic acid, in which case it should be washed with dilute ammonia water, then with water containing a few drops of hydrochloric acid.

Determination of Phosphorus by Fusion with Sodium Carbonate and Potassium Nitrate.

Fuse 2 grammes of the finely ground material with 12 grammes of sodium carbonate and 5 grammes of potassium nitrate; dissolve the fused mass in water and filter. Ignite and fuse the residue with a little sodium carbonate, dissolve and filter. Add to the first filtrate. Acidulate the filtrates with hydrochloric acid, heat to expel carbon dioxide and redissolve the precipitated tungstic acid with ammonia. Cool the solution in ice water, add magnesia mixture (page 54) and one-tenth of the volume of strong ammonia, stir vigorously at intervals for an hour or more and allow to stand over night. The volume should not exceed 400 c.c. Filter, wash with dilute ammonia and dis-

solve the precipitate in 1 to 6 hydrochloric acid and water, washing with the same strength of acid. Receive the filtrate and washings in a 400 c.c. beaker, add quinine hydrochloride, heat to boiling and allow to cool. Filter off any precipitated tungstic acid and wash with the acid wash-water containing 1 gramme quinine hydrochloride to the litre. To the filtrate add solution of ferric chloride containing 50 to 100 milligrammes of iron, add a slight excess of ammonia and boil. Filter and wash the precipitate of ferric oxide and phosphoric acid with boiling water. Dissolve in 25 c.c. of nitric acid diluted with hot water and wash the filter with water, receiving the filtrate and washings in an Erlenmeyer flask. Boil with potassium permanganate to destroy any quinine present. Precipitate with molybdate solution and determine the phosphorus as directed on page 93.

By Solution in Nitric and Hydrofluoric Acids.

Treat 2 grammes of the finely ground material in nitric and hydrofluoric acid and proceed as directed for the determination of tungsten until the fitrate from the precipitation by quinine hydrochloride is obtained. To this filtrate add ferric chloride solution and proceed as in the last method.

Determination of Silicon.

If silicon alone is to be determined, fuse 1 gramme with 8 grammes sodium carbonate and 2 grammes potassium nitrate. Treat the fused mass with hot water, wash it into a porcelain dish, acidulate with hydrochloric acid and evaporate to dryness. Cool, add 20 c.c. strong hydrochloric acid and evaporate again to dryness. Cool, add hydrochloric acid and water, filter, wash with 1 to 6 hydrochloric acid and water, dry, ignite and weigh. Treat the weighed precipitate with 2 drops of sulphuric acid and a few c.c. hydrofluoric acid, evaporate to dryness, ignite and weigh. The difference in weights is silica which contains 46.93 per cent. silicon. When sulphur is determined the silicon may be obtained from the same portion by igniting the tungstic acid filtered off as described in that method and getting the loss by treatment with hydrofluoric acid as described above. To this must be added the silica remaining in the residue which should be determined in the usual way.

Determination of Aluminum

Fuse 2 grammes of the material as in the determination of suphur. Dissolve in water and filter. Allow the filtrate and washings to run into a platinum dish. Nearly neutralize the solution in the dish with nitric acid and evaporate to about 75 c.c. Add ammonium nitrate either in the form of crystals or in a strong solution in small portions, boiling off all smell of ammonia after each addition, until the addition causes no effervescence. Evaporate to about 50 c.c., add a few drops of ammonia, dilute to 200 c.c., boil for a few minutes and filter. Wash the precipitate thoroughly with hot water, dry and ignite, adding to it the oxide of iron, etc., from the original fusion. Fuse the precipitate with a few grammes of potassium bisulphate. Dissolve the fused mass in 50 c.c. of hydrochloric acid and water 1 to 6, heat to boiling and add .2 to .3 gramme of quinine hydrochloride to precipitate any tungstic acid in the solution. Boil for a minute or two and allow to stand until perfectly cold. Filter on a double filter and wash with the hydrochloric acid quinine wash water (page 219).

Precipitate the oxide of iron and alumina in the filtrate with ammonia, filter and wash with hot water containing a little ammonium chloride. Dissolve the precipitate in hot dilute hydrochloric acid, allowing the solution to run into a 250 c.c. beaker. Add ammonia to the solution, which should be about 150 c.c. in volume, until a slight permanent precipitate of ferric hydrate forms; redissolve this by adding hydrochloric acid drop by drop. When the precipitate dissolves add 2 to 3 drops in excess and heat to boiling. Add ammonium bisulphite until the solution becomes colorless and smells of sulphurous acid, then add 2 or 3 c.c. of phenylhydrazine, which will precipitate the alumina immediately. Add 1 or 2 c.c. more of phenylhydrazine and a little filter paper pulp, stir vigorously and allow the precipitate to settle. Filter at once and wash four or five times with cold water, filling the filter full each time and allowing it to drain thoroughly after each washing.. Wipe any adhering precipitate from the beaker with a little filter paper and ignite. Treat the ignited precipitate with hydrofluoric and a drop of sulphuric acid, evaporate to dryness, ignite and weigh as Al_2O_3, which multiplied by .5303 gives the aluminum. Fuse the precipitate with a little sodium carbonate, dissolve in dilute nitric acid and test for phosphoric acid with molybdate solution. If any is present, determine it and subtract the phosphoric acid obtained from the alumina before calculating the aluminum.

Determination of Copper.

Dissolve 2 grammes of the sample in nitric acid and hydrofluoric acids, page 217, using as little hydrofluoric acid as possible. Dissolve 10 grammes of citric acid in 200 c.c. water in a 600 c.c. beaker and pour the solution of the sample into it. Make the solution slightly alkaline with ammonia and then acidulate with hydrochloric acid and add 5 c.c. in excess. Make the solution up to 500 c.c. and pass hydrogen sulphide into it cold until saturated. Filter, wash with hydrogen sulphide water, then once with dilute ammonia and then with cold water. Ignite the precipitate, dissolve it in nitric acid, add a few drops of sulphuric acid and precipitate by electrolysis.

Determination of Manganese.

Manganese may be determined in the residue from the solution in water of the fusion for sulphur or phosphorus. If the aqueous solution is colored by manganese add a few drops of hydrogen peroxide or a little filter paper pulp which will precipitate the manganese. Ignite the residue in the crucible in which the fusion was made and fuse with a small amount of potassium bisulphate. Dissolve the fused mass in 1 to 3 nitric acid and water. Transfer to an Erlenmeyer flask, make up to 60 to 70 c.c. with the same acid and determine the manganese by the bismuthate method.

Determination of Chromium and Vanadium.

Any chromium and vanadium present will be in the filtrate from the precipitation of tungstic acid by quinine hydrochloride in the determination of tungsten by solution in nitric and hydrofluoric acids, page 217. Evaporate this solution and heat until the excess of sulphuric acid is driven off, dissolve in 10 c.c. 1 to 2 hydrochloric acid, dilute with hot water and precipitate boiling by a sight excess of barium chloride. Filter off the barium sulphate, evaporate the filtrate to syrupy consistency and make an ether separation. The acid solution will contain the chromium, vanadium (aluminum and copper), and the ethereal solution any molybdenum that may be in the material. These may be determined by the methods described for the determination of vanadium, molybdenum, chromium, etc., page 202.

Determination of Carbon.

The carbon may be determined by direct combustion in oxygen as described on page 127.

Determination of Iron.

Iron may be determined in the residue from the solution in water of the fusion for sulphur or phosphorus by drying, igniting and fusing it with potassium bisulphate. Dissolve this fused mass in sulphuric acid and water, pass the solution through the reductor, page 89, and titrate with permanganate.

TUNGSTEN POWDERS.

The various elements present in this material may be determined by the methods described for the analysis of ferro-tungsten.

Determination of Sodium Tungstate.

Boil 2 to 3 grammes of the powder in 100 c.c. of water, filter, acidulate the filtrate with a few drops of nitric acid and precipitate the tungsten with mercurous nitrate and mercuric oxide, filter, wash, ignite and weigh as tungstic acid. The amount so obtained multiplied by 1.267 gives the sodium tungstate. Besides the sodium tungstate, tungsten powders generally contain, according to Brearley & Ibbotson (Analysis of Steel Works Materials, page 155), varying amounts of tungsten bronze. These small red, yellow or blue crystals may be noticed after boiling the powder in sodium hydroxide and they give the colors and composition of four sodium tungsten bronzes as follows:

Color	Composition	Per Cent Sodium
Purple-red	Na_2 $3WO_3$	6.20
Red-yellow	$2Na_2$ $5WO_3$	7.35
Golden-yellow	$5Na_2$ $12WO_3$	7.63
Blue	Na_2 $5WO_3$	3.81

No exact method is known for the determination of the amount of bronzes in tungsten powder or ferro-tungsten. Brearley and Ibbotson suggest the determination of soda after subtracting the soda found as sodium tungstate from the total soda found, calculating the remainder to tungsten bronze, according to the table of compositions given above. As the different bronzes vary so very much in their composition, this can be only an approximation and in most cases the sum of the elements found fall short of 100 per cent.

Determination of Soda.

Treat 2 grammes of the finely ground material in a platinum dish with 50 c.c. nitric acid, 1.2 sp. gr., add hydrofluoric acid, a little at a time, until solution is complete. Add 5 c.c. strong sulphuric acid and evaporate until the sulphuric acid fumes freely. Cool, add a little water and evaporate again until the mass is nearly dry in order to get rid of the hydrofluoric acid. Add 100 c.c. water and 5 c.c. of hydrochloric acid and boil vigorously. Filter, wash with hot water and acid, receiving the filtrate and washings in a platinum dish and evaporate again to dryness. Add 50 c.c. of water, and if any insoluble matter remains, filter and wash. To the filtrate add a clear solution of barium hydroxide until the sulphuric acid is precipitated and the solution is strongly alkaline to litmus. Boil, add ammonium carbonate to precipitate the excess of barium, boil until the smell of ammonia has gone, filter and wash with hot water. Evaporate to dryness, heat to dull redness, cool, and dissolve the residue in a few c.c. of hot water. Filter into a weighed crucible, using a very small filter paper, evaporate to low bulk and add a few drops of hydrochloric acid to convert the sodium carbonate to chloride. Evaporate to dryness, heat to dull redness and weigh as sodium chloride, which contains 53.077 per cent. of soda. Occasionally it contains a small amount of potash, but this need not be considered. Subtract the soda found as sodium tungstate from the total soda and multiply the remainder by 0.743 for the sodium. If we take the percentage of sodium obtained and multiply it by 15, we shall get an approximate idea of the amount of bronze in the material. The amount of tungstic acid in the bronze is found by subtracting the soda Na_2O, which has been calculated to sodium, from the amount of the bronze. This amount, with the amount of tungstic acid in the sodium tungstate and the amount present as tungstic oxide, must be added together and subtracted from the total tungstic acid found and the remainder calculated to tungsten.

A direct determination of oxygen by heating in a current of hydrogen is of little value, as neither the tungstic acid in the sodium tungstate nor that in the tungsten bronzes is reduced.

Determination of Tungstic Oxide.

All tungsten powders contain besides sodium tungstate varying amounts of oxides of tungsten. These cannot be accurately determined, but an

approximate estimation may be made by the method suggested by Brearley and Ibbotson (The Analysis of Steel Works Materials, page 153). Digest 3 grammes of the powder with 30 c.c. strong hydrochloric acid for a few minutes with constant stirring, dilute and pour the solution through a small filter, wash by decantation with hot water, evaporate the solution nearly to dryness and replace the hydrochloric with nitric acid. Boil the residue left in the beaker for 5 or 10 minutes with 50 c.c. binormal sodium hydroxide, filter through the filter used for the former filtration, which is now a nitric acid solution. Acidulate with nitric acid, boil and precipitate the tungstic acid by mercurous nitrate and mercuric oxide, ignite and weigh as WO_3. Subtract from this the amount of tungstic acid found in the sodium tungstate, determined by the method previously given, and the residue is the amount of tungstic acid existing as oxide. Some of this exists as the lower oxides of tungsten, but there will probably remain some oxide which cannot be determined by any known method.

THE ANALYSIS OF FERRO-MOLYBDENUM AND MOLYBDENUM METAL.

Ferro-Molybdenum.

Ferro-molybdenum is decomposed readily by acids but it is difficult to decompose it entirely by fusion with sodium carbonate and potassium nitrate or sodium peroxide, so that the best method of procedure is as follows: Treat one gramme of the finely powdered material in a large platinum crucible with 1 to 1 nitric acid and water. When the violent action has ceased, add 2 to 3 c.c., 1 to 3 sulphuric acid and water and evaporate nearly to dryness. The molybdenum dissolves readily in sulphuric acid and it is easy to see when the material is perfectly decomposed. Add 10 to 15 grammes of sodium carbonate to the mass in the crucible and heat until perfectly fused. Dissolve in hot water and filter, wash the residue of ferric oxide with hot water containing a little sodium carbonate and make up the solution to 500 c.c. Take 100 c.c. of this solution equal to .2 gramme of the material, heat to boiling and add 2 grammes of tartaric acid. Boil the solution until the tartaric acid is dissolved, then acidulate with 1 to 3 sulphuric acid and

water and boil until the carbonic acid is expelled. Cool the solution, add 2 to 3 drops of phenolphthalein solution, then add a solution of sodium hydroxide until the pink color remains and add 1 to 3 sulphuric acid and water until the pink color disappears and add 3 to 5 drops in excess. Dilute with cold water to 500 c.c. and pass hydrogen sulphide through the solution for about 30 minutes. The solution gradually turns red in color, sometimes dark red, but remains clear. Now add 5 to 6 c.c. 1 to 3 sulphuric acid and water and the molybdenum sulphide is precipitated. Pass the current of hydrogen sulphide for a few minutes, then heat the solution nearly to boiling and allow it to cool while the current of hydrogen sulphide still passes. Remove the tube from the beaker and allow the precipitate to settle. The supernatant fluid should be colorless, but if it should be blue it shows that some of the molybdenum has been reduced and as no sulphide of this molybdenum salt exists the operation is a failure and another portion must be taken for the analysis. If the directions above given are carefully followed this should never occur.*

Filter and wash with hydrogen sulphide water containing a few drops of dilute sulphuric acid. Remove the filter containing the precipitate from the funnel, spread it out on the side of the beaker in which the precipitation was made and wash the precipitate from the filter with a jet of hot water. Remove the last traces of the precipitate from the filter by pouring over it 40 c.c. of hot dilute sulphuric acid 1 to 3, to which a little nitric acid has been added. Add 20 c.c. of nitric acid and boil the solution down until all the sulphur has been oxidized and heat it until the sulphuric acid fumes. Cool, dilute to 50 c.c. and add an excess of a strong solution of potassium permanganate, boil until the permanganate is decomposed, add sulphurous acid to dissolve the precipitated manganese dioxide and boil until all traces of sulphurous acid are expelled. Cool, dilute to about 200 c.c. with cold water and pass the solution slowly through the reductor, page 89. Titrate with standard permanganate solution. The solution as it comes through the

*This method of precipitation is due to Mr. Charles Morris Johnson, Chemical Analysis of Special Steels, etc., 2nd ed., page 116. He does not mention the fact, although probably aware of it, that if the solution is acidulated by sulphuric acid before adding the tartaric acid it is almost impossible to avoid reducing some of the molybdenum with the consequent appearance of the blue color after precipitating with hydrogen sulphide. Whereas, if the tartaric acid is added first to the alkaline solution this practically never occurs.

reductor should be bright green in color and the reduction is to $Mo_{24}O_{37}$ and the value of the permanganate solution in iron multiplied by .58709 gives the molybdenum.

Instead of dissolving the precipitate of molybdenum sulphide it may be dried and the filter and precipitate ignited at a very low temperature until the paper is burned. The temperature must not at any time be allowed to get beyond a faint red. When the ignition is finished, cool and weigh the nearly white precipitate of molybdenum trioxide. Dissolve in hot dilute ammonia, filter and wash. Burn the filter in the crucible in which the ignition was made and subtract from the first weight. The difference is MoO_3, which contains 66.67 per cent. molybdenum. There is always a slight loss by this method amounting generally to .1 to .2 per cent.

The precipitation of the molybdenum sulphide may be made in a pressure bottle after preparing the solution as directed above, and the precipitate filtered and weighed on a Gooch crucible as directed on page 205.

Determination of Silcon, Tungsten and Vanadium.

Treat 2 grammes of the finely ground material in a 400 c.c. beaker with 20 c.c. nitric acid 1.2 sp. gr. When the action has ceased, add 20 c.c. hydrochloric acid and evaporate to dryness at a temperature not much above 100 c.c. Add 20 c.c. hydrochloric acid and evaporate as before. Add 20 c.c. hydrochloric acid and heat until the iron is dissolved, then add 100 c.c. water and boil for a few minutes. All the tungstic acid will remain insoluble. Filter, wash with hydrochloric acid and water 1 to 6. If any tungstic acid adheres to the beaker, dissolve it in ammonia, wash the solution into a crucible, evaporate to dryness, place the filter containing the tungstic acid in it, ignite and weigh. Treat the residue with hydrofluoric acid and a few drops of sulphuric acid, evaporate to dryness, ignite and weigh. The loss is Silica. Then proceed as on page 196 for the determination of tungsten, etc.

Evaporate the filtrate from the tungstic acid which contains the molybdenum and vanadium to syrupy consistency after adding to it 3 grammes of iron in the form of ferric chloride. Make an ether separation as directed on page 202. Evaporate the acid solution after adding 2 grammes more of iron in the form of ferric chloride, and make another ether separation. The molybdenum will all be in the ethereal solution and the vanadium in the acid solution. Determine the vanadium as directed on page 203.

Determination of Chromium.

When chromium is present it may be separated from the vanadium in the acid solution obtained above by changing the hydrochloric to nitric acid and proceeding as directed for the separation of vanadium from chromium as described on page 203.

Determination of Manganese.

The manganese will be with the chromium when it is separated from the vanadium as directed above and is determined as described on page 203. If manganese alone is to be determined, treat 2 grammes of the material in a large platinum crucible with nitric acid, evaporate to dryness and fuse with 10 grammes of sodium carbonate. Treat the fused mass with hot water, boil, add a few drops of hydrogen peroxide or a little sodium peroxide to reduce any manganese in the solution, filter and wash with water containing a little sodium carbonate. Dissolve the precipitate of oxide of iron and manganese in sulphurous acid and determine the manganese as directed on page 204.

Determination of Iron.

Treat 1 gramme as for the determination of silicon, tungsten and vanadium, and after filtering off the tungsten dilute the filtrate to about 500 c.c. with hot water, add an excess of ammonia and boil. Filter, wash with hot water, redissolve in dilute hydrochloric acid, reprecipitate by ammonia, filter and wash. Dissolve the precipitate in hot dilute sulphuric acid, boil, add a little potassium permanganate to destroy organic matter, pass the solution through the reductor and titrate with permanganate. The solution that passes through the reductor should be colorless. If there is the least tinge of green color it shows that all the molybdenum has not been separated from the iron and the determination should be repeated, making a third precipitation with ammonia to get rid of the last trace of molybdenum. If the sample contains vanadium the greater part of it will be carried down with the oxide of iron and it will be necessary to dissolve the oxide of iron in nitric acid instead of sulphuric acid in the method as described above, evaporate almost to dryness and drop the diluted solution into a solution of sodium hydroxide exactly as described for the determination of vanadium on page 203. Ignite the two precipitates obtained by this method

in a platinum crucible and fuse with a little potassium bisulphate. Dissolve the fused mass in water, add a few drops of sulphuric acid and pass the solution through the reductor and titrate.

Determination of Sulphur.

Treat 1 to 2 grammes of the material with 20 to 30 c.c. of strong nitric acid in a 600 c.c. beaker and evaporate twice to dryness with an excess of hydrochloric acid. Dissolve in hydrochloric acid, dilute with 6 times the volume of acid with water, boil, filter and wash with dilute hydrochloric acid, 1 part acid to 6 parts of water. Partly neutralize with ammonia, boil and precipitate by barium chloride. Allow to stand over night, filter, wash first with water containing a little hydrochloric acid and then with water containing a little ammonia and finally with cold water. Ignite and weigh as barium sulphate. If the precipitate is not white, fuse with a little sodium carbonate, dissolve in hot water, filter and wash. Acidulate the filtrate with hydrochloric acid and reprecipitate with barium chloride.

Determination of Phosphorus.

Treat 2 grammes of the material with nitric and hydrochloric acids as directed for the determination of silicon, tungsten and vanadium on page 226, and after filtering from the silica and tungstic acid add to the filtrate 10 grammes of citric acid and an excess of ammonia. Cool the solution, which should not exceed 200 c.c. in volume, in ice water, add magnesia mixture and stir vigorously. Proceed as directed for the determination of phosphorus, pages 218 and 219, but after igniting the precipitate of ammonium magnesium phosphate dissolve it in nitric acid and precipitate by molybdate solution, filter and titrate the ammonium phospho-molybdate.

Instead of adding citric acid to the solution as directed above, precipitate the iron by ammonia, using only a slight excess and boil for a few minutes. Filter, wash the precipitate with hot water, dissolve in hydrochloric acid and repeat the precipitation. Filter, wash, dissolve in dilute hot nitric acid and precipitate by molybdate solution. As the vanadium is nearly all with the iron, neutralize the nitric acid solution and cool, add 5 c.c. of a saturated solution of ferrous ammonium sulphate before adding the molybdate solution, page 93.

Determination of Carbon.

Carbon is readily determined by direct combustion in oxygen.

THE ANALYSIS OF MOLYBDENUM METAL.

Determination of Molybdenum.

Treat 1 gramme of the material in a large platinum crucible with nitric acid, add a few drops of sulphuric acid, evaporate to dryness and fuse with 20 grammes of potassium bisulphate. Treat the fused mass with water, add an excess of ammonia, which will dissolve everything but a little oxide of iron, and make up to a litre.

Filter through a dry filter, take two portions of 100 c.c. each (representing 0.1 gm. of the material). Acidulate with sulphuric acid, run through the reductor and titrate as directed on page 225. The value of the permanganate solution in iron multiplied by .58709 gives the molybdenum. The two portions should give practically the same result.

Determination of Carbon.

Determine the carbon by direct combustion in oxygen in a quartz or porcelain tube as the molybdenum volatilizes quite freely. By mixing a half factor of iron with a half factor of the metal the volatilization will be avoided.

The other elements are determined in the manner directed for their determination in ferro-molybdenum.

THE ANALYSIS OF FERRO-VANADIUM.

Determination of Vanadium.

Ferro-vanadium is readily decomposed by nitric acid in the cold, but upon heating the vanadic acid crystallizes out and it is necessary to add hydrochloric acid to get it into solution. Treat 1 gramme of the finely ground sample with nitric acid and add hydrochloric acid until the solution is complete. Evaporate to dryness twice with hydrochloric acid to get rid of the nitric acid, being careful not to heat it above 100° C., as the vanadium is volatile at higher temperatures. Add hydrochloric acid and evaporate to syrupy consistency. Take it up with hydrochloric acid 1.1 sp. gr., cool in ice water, add 5 to 10 drops of sulphurous acid and separate by ether. Determine the vanadium as directed on page 198.

Determination of Tungsten and Silicon.

Tungsten and silicon are determined exactly as in the determination of these elements in ferro-molybdenum.

Determination of Molybdenum.

The molybdenum will all be found in the ethereal solution with the iron and is determined as directed for the determination of molybdenum in steel.

Determination of Chromium.

Treat 2 grammes of the material exactly as directed for the determination of vanadium until the solution in hydrochloric acid is complete, dilute to about 400 c.c. with water, add an excess of ammonia and boil. Filter, wash with hot water, dry and ignite the precipitate.

Fuse 2 to 3 grammes of sodium carbonate in a small platinum crucible and run it up on the sides to line it. Mix the precipitate with a little sodium peroxide and fuse as directed on page 185. Dissolve in water and boil vigorously. Filter, if the filtrate is colorless no chromium is present, if very faintly yellow determine the amount by color as directed on page 186, but if an appreciable amount is shown by the color, acidulate by sulphuric acid and determine the amount as directed on page 185.

Determination of Silicon.

Silicon is determined by treating 2 grammes of the material as directed for the determination of vanadium by filtering the insoluble matter after evaporating the solution to dryness. Ignite, weigh and treat with hydrofluoric and sulphuric acids. The loss of weight is silica, which contains 46.93 per cent. silicon.

Determination of Sulphur.

The solution filtered from the insoluble matter as described above is diluted to about 250 c.c., nearly neutralized, heated to boiling and 25 c.c. of a solution of barium chloride added. After standing over night, filter, ignite and weigh the barium sulphate. The solution must not be too nearly neutralized or a precipitate of barium vanadate may contaminate the barium sulphate.

Determination of Phosphorus.

Treat 2 grammes of the material as directed for the determination of silicon. After filtering off the silica, add to the filtrate about 10 grammes of citric acid and an excess of ammonia and proceed as directed for the determination of phosphorus in ferro-molybdenum.

Determination of Manganese.

The manganese will be found in the insoluble matter from the fusion of the precipitate for the determination of chromium if the precipitation is made by sodium hydroxide instead of ammonia, and the manganese may be determined by dissolving this precipitate in sulphurous acid as directed on page 204.

Determination of Iron.

Fuse 1 gramme of the finely ground material with 20 grammes of sodium carbonate and 3 grammes of potassium nitrate. Treat the fused mass with hot water, boil, filter and wash thoroughly with hot water. Ignite the precipitate and fuse again with 10 grammes of sodium carbonate. Dissolve in water and filter. Ignite the precipitate and fuse with 10 grammes of potassium bisulphate. Dissolve in hot water with the addition of a few drops of sulphuric acid, pass through the reductor and titrate with permanganate.

Determination of Carbon.

The carbon is best determined by direct combustion in oxygen.

THE ANALYSIS OF FERRO-CHROME.

Determination of Chromium.

Fuse 10 to 15 grammes of sodium carbonate in a 30 c.c. platinum crucible, hold the crucible firmly in the tongs and by a rotary movement spread the sodium carbonate around the inside of the crucible so that when cold the crucible will be lined evenly about three-fourths of the way up with the sodium carbonate. The lining should be a little thicker on the bottom than on the sides. Place about 10 grammes of sodium peroxide in the crucible, add 0.5 gramme of the finely ground ferro-chrome and mix as thoroughly as possible with a platinum wire. Place the crucible over a low light and

heat carefully until the sodium peroxide is melted. Allow it to remain melted for about 3 minutes but do not raise the temperature. It is never necessary to heat the crucible above low redness on the bottom. With proper care the lining of sodium carbonate will not be melted and the crucible will not be attacked as much as with an ordinary soda nitre fusion.

Run the melt well up in the lining and allow it to cool. Place the crucible in an empty 600 c.c. beaker and add a little cold water from a wash bottle covering the beaker with a watch glass to avoid loss from the effervescence caused by the escape of oxygen from the sodium peroxide. By stirring the mixture in the crucible with a glass rod and adding cold water from time to time the flux will be entirely dissolved in a few minutes. Remove the crucible and wash its contents into the beaker with hot water. It may be necessary to boil the water in the crucible to remove the last traces of the lining. Boil the contents of the beaker, about 250 c.c. in volume, for 20 minutes to thoroughly decompose the sodium peroxide. Filter, preferably through an alundum plate, as this avoids any reduction of the chromic acid by the organic matter of filter paper and make the solution up to 500 c.c. in a carefully calibrated flask. Mix thoroughly and divide into two portions of 250 c.c. each. Dilute each portion to 700 c.c. and add 50 c.c. of sulphuric acid and water 1 to 2. Boil to expel the carbon dioxide and cool to room temperature. To each portion add 4.1 grammes of pure ferrous ammonium sulphate, and titrate the excess with standard potassium permanganate. From the number of c.c. of the permanganate required to oxidize the 4.1 grammes of ferrous ammonium sulphate, subtract the number required to titrate the solutions above and the difference is the number of c.c. of the permanganate equivalent to the ferrous ammonium sulphate oxidized by the chromic acid in the solutions. The value of 1 c.c. of the permanganate in iron multiplied by .31041 is its value in chromium. Therefore multiply this value by the number of c.c. found above and the result by 4 and the product is the chromium in one gramme of the ferro-chrome.

The results on the two portions should agree to within .1 to .2 of a cubic centimetre. The green color of the solutions makes the end of the reaction with the permanganate a little difficult to detect at first, but experience will soon teach the analyst to observe the change from green to a purplish shade that indicates the proper point. For this reason it is well in titrating the

ferrous ammonium sulphate to add enough of a solution of chromous sulphate to give the solution a tint about as strong as that observed in the determination of the chromium in an average ferro-chrome. Instead of filtering off the insoluble matter from the fusion some analysts prefer to add sulphuric acid (after boiling to decompose the sodium peroxide) to dissolve the residue and decompose the sodium carbonate at the same time. Analyses of samples by the two methods give practically the same results unless the unfiltered solution is cloudy after boiling off the carbon dioxide. This is generally due to the presence of manganese in the form of dioxide which will oxidize some of the ferrous ammonium sulphate and give too high a result. This solution must therefore be filtered before adding the ferrous ammonium sulphate.

Mr. Frederick Wynkoop has made a number of experiments on the use of nickel and iron crucibles. He showed that when 8 grammes of sodium peroxide was fused in a nickel crucible and treated exactly as if ferro-chrome were present, the solution acidulated with sulphuric acid gave a pink instead of a green solution and oxidized ferrous ammonium sulphate exactly like chromic acid, owing probably to the formation of a small amount of nickelic sulphate which is not decomposed by sulphuric acid. When an iron crucible was used the same result was found, due probably to the formation of a small amount of ferrate in the large amount of iron oxidized. The amount of ferrous ammonium sulphate oxidized corresponded to from .3 to .5 of a per cent. of chromium. In the case of the nickel crucible the oxidation of the ferrous ammonium sulphate was equivalent to from .6 to 1.0 per cent. of chromium.

Determination of Aluminum.

Fuse 1 to 2 grammes with sodium peroxide as directed above. Treat with hot water, boil and filter. If the ferro-chrome is high in iron it is necessary to ignite and fuse the insoluble matter with sodium carbonate and a little potassium nitrate, dissolve and filter as before. Combine the filtrates and boil down in a platinum dish with additions of ammonium nitrate until further additions of ammonium nitrate cease to cause evolution of ammonium carbonate. When the solution is down to a volume of about 50 c.c. add a few drops of ammonia, dilute to 200 c.c. filter and wash with hot water containing a little ammonium nitrate. Dissolve the precipitate in hydro-

chloric acid, allowing the solution to run into a 250 c.c. beaker, and wash the filter with hot water. Dissolve the insoluble oxide of iron from the fusions of the ferro-chrome obtained as described above in hydrochloric acid, allowing the solution to run into the 250 c.c. beaker containing the solution of the precipitate obtained by evaporating with ammonium nitrate. Evaporate the combined filtrates to dryness to get rid of the silica and precipitate the alumina by phenylhydrazine as directed on page 192.

Determination of Manganese.

When fusing a portion of the material for the determination of chromium, the manganese will all be in the matter insoluble in water and may be determined exactly as directed for the determination of manganese in ferro-tungsten, page 221.

Determination of Silicon and Sulphur.

Fuse 1 gramme of the finely ground material with sodium peroxide in a lined crucible as directed for the determination of chromium, using an alcohol lamp. Treat the fused mass with water and when thoroughly disintegrated, acidulate with hydrochloric acid and evaporate to dryness in a porcelain dish. Add strong hydrochloric acid to the fused mass and evaporate a second time. Add 20 c.c. strong hydrochloric acid, heat for a few minutes, then add enough water to dissolve the soda salts, filter and wash. Ignite and weigh the insoluble matter, treat with hydrofluoric and sulphuric acids, ignite and weigh. The loss is silica which contains 46.93 per cent. silicon. Nearly neutralize the filtrate, boil and precipitate the sulphuric acid with barium chloride and determine the sulphur with the usual precautions.

Determination of Phosphorus.

Fuse 1 gramme as for the determination of sulphur. Treat with water, boil thoroughly and filter. If the fusion is properly made all the phosphorus will be in the filtrate, but it is safer to ignite the insoluble matter and fuse it with potassium bisulphate, dissolve in hydrochloric acid and water. precipitate by a slight excess of ammonia, filter and wash with hot water. Dissolve the precipitate in dilute nitric acid and test for phosphoric acid in

the usual way with molybdate solution. To the filtrate (which should be in a platinum or porcelain dish), containing the chromic and phosphoric acids, add a solution of alumina in sodium hydroxide made by dissolving 50 to 100 milligrams of metallic aluminum in 1 gramme of sodium hydroxide and a little water. Evaporate to low bulk, adding ammonium nitrate from time to time until the sodium carbonate is converted to nitrate and the addition of ammonium nitrate causes no further effervescence and the solution smells only faintly of ammonia. Dilute with hot water, filter and wash. Dissolve the precipitate of alumina, which will contain all the phosphoric acid, in dilute nitric acid, allowing the solution and washings to run into a 250 c.c. Erlenmeyer flask, nearly neutralize with ammonia, precipitate by molybdate solution and determine the phosphorus in the usual way.

Determination of Iron.

Fuse .5 gramme as directed for the determination of chromium, treat the fused mass with water and filter. Ignite the insoluble matter and fuse with potassium bisulphate. Dissolve in water with the addition of 5 c.c. of sulphuric acid, pass the solution through the reductor and titrate with permanganate.

Determination of Carbon.

Weigh carefully .5 gramme of the finely ground material, add a factor weight (2.7273 grammes) of fine drillings of ingot iron, mix thoroughly in the pan and transfer the material to the depression in the alundum in the platinum boat, page 129. Finish the determination as directed for the direct combustion in a current of oxygen, page 127, *et seq.* Subtract from the weight of the CO_2 the amount due to the carbon in the iron and calculate the carbon on the .5 gramme of the material. The "Armco" iron of the American Rolling Mill Company is admirably adapted for this purpose. The drillings should be small and sharp; those taken with a diamond-pointed drill at very slow speed are best. This iron contains from 0.010 per cent. to 0.018 per cent. carbon and the factor weight gives a subtraction of 0.0010 to 0.0018 gramme from the weight of the CO_2 found. This method gives excellent results on all grades of ferro-chrome.

THE ANALYSIS OF FERRO-SILICON.

Determination of Silicon.

Many low-grade ferro-silicons may be decomposed by acids and some that resist boiling acids are decomposed by keeping the acid cold. To one gramme of the finely ground material add 50 c.c. of strong hydrochloric acid and 5 c.c. of strong nitric acid. Do not allow the liquid to get hot. Add small amounts of nitric acid from time to time until the decomposition seems to be complete. Heat gently for a few minutes, dilute, filter and wash thoroughly. Evaporate the filtrate to dryness, moisten with strong hydrochloric acid and evaporate a second time. Add hydrochloric acid and when the iron is dissolved, dilute, filter and wash. Ignite the two precipitates very carefully to avoid loss of silica and when the paper is thoroughly burned, heat at the highest temperature of the Bunsen burner, keeping the crucible covered, cool, and weigh. Treat the silica with hydrofluoric and sulphuric acids, ignite, and weigh. The difference is silica which contains 46.93 per cent. silicon. Occasionally small particles of carborundum (C Si) may remain in the crucible. If any oxide of iron is also present, this may be dissolved in hydrochloric acid and the carborundum filtered off and weighed.

Ferro-silicon insoluble in acids must be decomposed by fusion. Mix thoroughly in a platinum crucible 1 gramme of the material with 20 grammes of sodium carbonate and 4 grammes of potassium nitrate previously ground together and fuse at as low a temperature as possible until the fused mass is tranquil, run well up on the sides of the crucible and when cool, dissolve the fused mass in hot water and wash it out into a porcelain dish. Dissolve the stain in the crucible in hydrochloric acid and wash it into the dish. Acidulate the solution in the dish with hydrochloric acid and evaporate to dryness. Moisten the cooled mass with hydrochloric acid and evaporate again to dryness. The strong acid helps to dehydrate the silica and the second evaporation occupies very little time. Warm with strong hydrochloric acid, add enough water to dissolve the salts, filter and wash thoroughly with hot water. For very accurate work it is necessary to evaporate the filtrate to dryness, dissolve as before, filter and wash, although when the operation is conducted as directed above appreciable amounts of silica are rarely found in the solution. Ignite the filters very carefully to avoid loss of

silica by the gases from the paper, and when thoroughly burned, cool and moisten the silica with a few drops of dilute sulphuric acid, evaporate the sulphuric acid, ignite strongly and weigh. Treat with hydrofluoric and sulphuric acids, evaporate to dryness, ignite and weigh. The loss is silica which contains 46.93 per cent. silicon. As pointed out by Gooch, moistening the silica with sulphuric acid converts any sodium chloride which may remain with the silica to sodium sulphate and avoids any error occasioned by the subsequent treatment with hydrofluoric and sulphuric acids. Instead of fusing with sodium carbonate and potassium nitrate proceed as follows: Line a platinum crucible with 10 to 15 grammes of sodium carbonate (see page 231) and when cold place 10 grammes of sodium peroxide in the crucible, add 1 gramme of the finely ground material and mix thoroughly with a platinum wire. Heat carefully until the mixture is fused and allow it to remain fused for three minutes. Run the fused mass up on the sides of the crucible, keeping it well below the lining. Place the cold crucible in a platinum or porcelain dish and add cold water carefully until the violent action is over. Wash the contents of the crucible into the dish and boil until the excess of sodium peroxide is decomposed. Dissolve any adhering residue in the crucible in hydrochloric acid, wash it into the dish, acidulate with hydrochloric acid and proceed as before.

Determination of Sulphur.

The filtrate from the silica can be used for the determination of sulphur, but if it is the fusion should be made over an alcohol lamp to avoid the possibility of contamination by the sulphur in the gas. Add ammonia to the solution until a slight precipitate of iron is formed which fails to dissolve by stirring. Add hydrochloric acid until the precipitate dissolves and 10 drops in excess. Heat to boiling, add 15 c.c. of a saturated boiling solution of barium chloride and stand aside for 12 hours. Filter, wash with cold water containing a few drops of hydrochloric acid, ignite and weigh as barium sulphate which contains 13.732 per cent. sulphur.

Determination of Phosphorus.

Heat 2 grammes of the sample in a platinum dish with 25 c.c. of nitric acid, 1.2 sp. gr., adding hydrofluoric acid in small portions until solution is

complete. Add 5 c.c. sulphuric acid and water 1 to 1 and evaporate until the sulphuric acid fumes freely. Cool, add 10 c.c. hydrochloric acid and heat until solution is complete. Dilute and wash the solution into a beaker. Precipitate by a very slight excess of ammonia, boil, filter and wash with hot water containing a little ammonium nitrate. Dissolve the precipitate in dilute hot nitric acid and precipitate the phosphorus by molybdate solution in the usual way.

Determinaton of Manganese.

The variation in the amounts of manganese in high silicon metals is very great, running from a few thousandths of a per cent. in high ferro-silicon to 20 per cent. in silicon spiegels. Dissolve one gramme of the material in a platinum dish in nitro-hydrofluoric acid, add 5 c.c. of sulphuric acid and evaporate until the sulphuric acid fumes freely. Dissolve in nitric acid and determine the manganese by the bismuthate method. When the amount of manganese is great, dilute to 500 c.c. and proceed as in ferro-manganese.

Determination of Aluminum, Calcium, Magnesium, Titanium and Chromium.

Dissolve 5 grammes in nitro-hydrofluoric acid, add 10 c.c. of sulphuric acid and evaporate until the sulphuric acid fumes freely, cool, add water to dissolve the sulphates, add a little more hydrofluoric acid and evaporate again to get rid of every trace of silicon. Dissolve in 50 c.c. of hydrochloric acid, 1.1 sp. gr., transfer to a beaker, dilute to 300 c.c. with hot water, add a little bromine water and precipitate with a very slight excess of ammonia. Boil for one or two minutes, filter and wash with hot water. Dissolve the precipitate of oxide of iron in hot dilute hydrochloric acid, precipitate by ammonia as before, boil one or two minutes, filter through the same filter and add this filtrate to the first. The precipitate contains the alumina, oxide of iron, titanic acid and manganese. The filtrate contains the lime and magnesia which are determined in the usual way.

Dissolve the precipitate of oxide of iron, etc., in hot dilute hydrochloric acid, receiving the solution and washings in a 400 c.c. beaker. Keep the filter which may contain a little titanic acid to ignite with the alumina later

on. Evaporate the solution to syrupy consistency and make an ether separation to get rid of the iron. The alumina, titanic acid and chromic oxide will be in the acid solution. Evaporate off the ether and precipitate the alumina, titanic acid and chromic oxide by phenylhydrazine as directed on page 192, and weigh. Fuse the precipitate with a little sodium carbonate and a pinch of sodium nitrate. Dissolve the fused mass in a little hot water and filter through a small filter into a tall 50 c.c. beaker or small cylinder and determine the chromium by color as directed on page 186. Ignite the filter with the filter preserved from the solution of the ferric oxide, etc., as noted above and fuse with a little potassium bisulphate, cool, add a few drops of strong sulphuric acid, heat until the fusion is liquid, cool and dissolve in water. Transfer the solution to a tall beaker or cylinder and dilute with cold water to about 50 or 75 c.c. In a similar beaker put about the same volume of water with a few drops of sulphuric acid. To the contents of each beaker add a few c.c. of hydrogen peroxide, and to the beaker containing the water add a standard solution of titanic acid until the yellow color of the sample is matched by the liquid to which the titanic acid solution is added, the volume of liquid in each being the same. The standard solution is prepared by fusing 100 m.g. of pure titanic acid in 10 grammes of potassium bisulphate, dissolving in water containing 5 c.c. of sulphuric acid and diluting to 100 c.c. One c.c. of this solution is equal to 1 m.g. of titanic acid, which contains 60.05 per cent. titanium. Subtract the titanic acid and chromic oxide previously obtained and the remainder is alumina which contains 53.03 per cent. of aluminum. If the sample contains an appreciable amount of phosphorus the precipitate of alumina, titanic acid and chromic oxide will contain nearly but not all the phosphorus as phosphoric acid. Experiments show that the amount is about 70 per cent. of the total amount and this may be subtracted from the alumina before calculating to aluminum. Or, as the phosphoric acid will all be in the sodium carbonate solution containing the chromic acid, this solution, after determining the chromium by color, may be acidulated by nitric acid, the phosphoric acid precipitated by molybdate solution and determined in the usual way. If the sample contains much manganese it will be necessary instead of precipitating the oxide of iron and alumina by ammonia, to neutralize with sodium carbonate and precipitate by sodium acetate. To the filtrate from the oxide of iron, etc., add

bromine to precipitate the manganese. Filter off the manganese dioxide and determine the lime and magnesia in the filtrate.

Determination of Carbon.

Carbon may be determined by direct combustion in oxygen. The heat generated by the oxidation of the silicon is so great that the silica formed unites with the alundum and oxide of iron, forming a silicate of alumina and ferric oxide, which fuses to the boat and cover. To avoid this difficulty it is best to burn 1 gramme of the sample with a factor weight of low steel, as directed for the determination of carbon in ferro-chrome, page 235.

THE ANALYSIS OF FERRO-MANGANESE AND MANGANESE METAL.

Determination of Manganese.

Fuse 1 gramme of the material in a large platinum crucible with 20 grammes of potassium bisulphate. If the potassium bisulphate is powdered and mixed thoroughly with the sample, the fusion will take place much more quickly than if the potassium bisulphate is in lumps. Heat very carefully, as the fusion is certain to boil, and to prevent loss it must be watched constantly. This is largely due to the escape of sulphur dioxide generated by the oxidation of the metals at the expense of the sulphuric acid, which causes the mixture to become basic and raises its fusion point. By directing the flame against the upper part of the crucible the fused mass is prevented from rising to the top of the crucible, and the decomposition of the sample is completed without danger of loss. Finally heat to full redness, run the fused mass well up on the sides of the crucible and allow it to cool. When cold the fused mass is readily detached from the crucible. Dissolve it in hot water with the addition of a little nitric acid and make the solution up to a litre. For ferro-manganese of 40 per cent. and over, measure 20 c.c. of the solution by means of a carefully calibrated pipette into an Erlenmeyer flask, add 20 c.c. of strong nitric acid and 40 c.c. of water and determine the manganese by the bismuthate method, page 116. It is best to measure two portions, the results on which should agree within 0.1 c.c. As the amount used is one-fiftieth of a gramme, the result must be multiplied by 50 for the percentage of manganese.

Determination of Carbon.

Mix 1 gramme of the material with a factor of ingot iron and make the combustion as directed for the determination of carbon in ferro-chrome, page 235.

The other elements are determined as in steel.

ANALYSIS OF FERRO-TITANIUM.

Determination of Titanium.

As phosphoric acid interferes with the precipitation of titanic acid, it is best to get rid of the phosphorus by fusing with sodium carbonate and nitrate. Fuse 1 gramme of the sample with 15 grammes of sodium carbonate and 2 grammes of sodium nitrate and dissolve in hot water. The sodium titanate formed is insoluble in water, but potassium titanate is not, so that sodium and not potassium nitrate is used. Filter and wash. Ignite the precipitate of ferric oxide and sodium titanate in the crucible in which the fusion was made and fuse with fifteen grammes of potassium bisulphate. Proceed as directed on page 172. As some platinum from the crucible is liable to be with the titanic acid precipitated, re-fuse this precipitate with 10 grammes of potassium bisulphate and dissolve the fused mass as in the first instance. Then pass hydrogen sulphide through the solution, filter and precipitate as before. This precipitate is generally perfectly pure and contains 60.05 per cent. titanium.

Determination of Silicon.

Fuse 1 gramme of the sample with 20 grammes of potassium bisulphate powdered and mixed with the sample.

ANALYSIS OF FERRO-PHOSPHORUS.

The analysis of ferro-phosphorus offers no special difficulties except in the determination of phosphorus. This element cannot be determined by the solution of the sample even in fuming nitric acid, as a large proportion of the phosphorus escapes oxidation. The only accurate method is fusion with sodium carbonate and sodium peroxide and care must be exercised even in the use of this method, as there is a strong tendency on the part of the ferro-phosphorus to melt into globules, unless it is thoroughly mixed with the peroxide, and thus make the decomposition very difficult.

Determination of Phosphorus.

Line a nickel crucible with 20 grammes of sodium carbonate. It will be necessary to use a blast lamp or a small furnace for this purpose, as the ordinary Bunsen lamp does not give sufficient heat to melt this amount of sodium carbonate in a nickel crucible. A platinum crucible cannot be used, as the long heating necessary to thoroughly decompose ferro-phosphorus causes too much action on the platinum. When the crucible is cold place in it 10 grammes of sodium peroxide and .5 grammes of the material ground as finely as possible in the agate mortar and mix thoroughly with a platinum rod. Heat cautiously until the sodium peroxide is melted and keep it melted for 15 minutes, but do not raise the temperature any higher than is necessary to keep the mass barely liquid. Run the fusion up on the sides of the crucible and cool. Place the crucible in a beaker and add cold water carefully until the violent action is over, then wash the contents of the crucible into the beaker. Clean the crucible with a little dilute nitric acid and pour it into the beaker, then add nitric acid until the solution is distinctly acid and the oxides of iron, nickel, etc., are dissolved. Then add 10 c.c. of nitric acid in excess and boil thoroughly, after adding 3 or 4 drops of hydrochloric acid. Cool the solution and make it up to 500 c.c. With a carefully calibrated pipette transfer 100 c.c. of the solution to an Erlenmeyer flask, add 25 c.c. strong nitric acid, 45 c.c. dilute ammonia, sp. gr. 0.96 and 100 c.c. molybdate solution, shake thoroughly and allow the precipitate to settle. Filter on a Gooch crucible and wash first with ammonium sulphate solution (page 92) and then with 3 per cent. nitric acid. Dry at 104° and weigh. The weight of the precipitate multiplied by .0163 gives the phosphorus in .1 gramme of the material.

METHODS FOR THE ANALYSIS

OF

IRON ORES

A FEW words in regard to the proper method of taking samples of iron ores may not be amiss, for unless the sample truly represents the lot from which it is taken, the subsequent work of the analyst is useless, if not misleading.

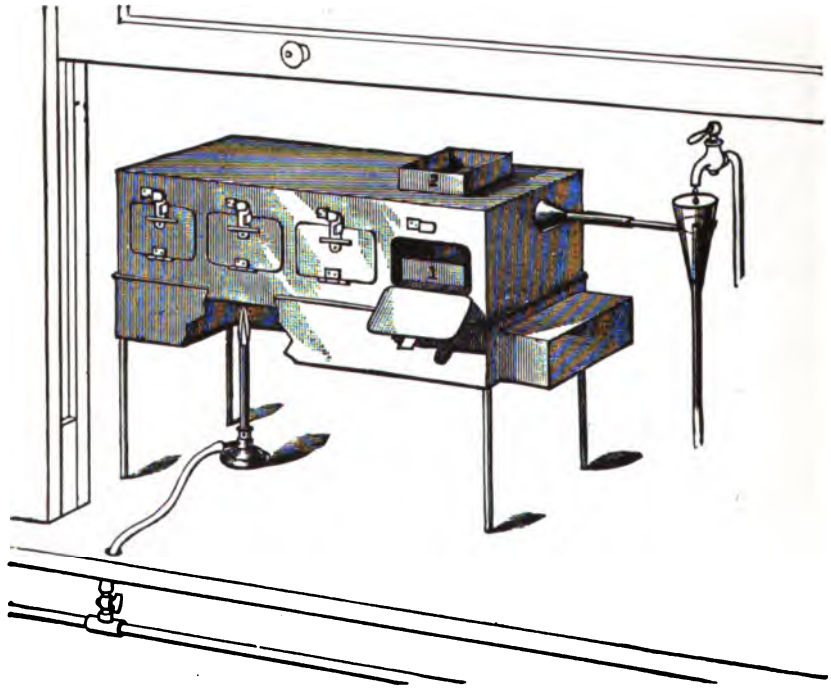
In drawing a sample, note carefully the relative amounts of fine ore and lumps in the lot to be sampled, and see that this proportion be observed in the whole amount taken. A small trowel may be used for taking the fine ore, and only about a teaspoonful should be picked up at one time. In taking pieces from the lumps, it will never do to merely chip the outside, but each lump as selected should be broken and chippings no larger than a cherry taken from both the inside and the outside. In sampling from cars or wagons these points should be observed in each car or wagon, for it is rarely the case that the ore even from one mine is so uniform as to render this precaution unnecessary. In some cases the lumps are covered with dirt or gangue, making the outside of the lump poorer in iron than the inside, and on the other hand the lumps are merely masses of dirt coated with ore. Then the fine stuff may be much richer than the lumps, or it may be merely dirt or gangue, while it almost always contains more hygroscopic water than the lumps. The sample should be taken in tin cans with close-fitting lids, and the amount should be proportioned to the size of the lot sampled. Two pounds to ten tons is a good rule for large lots.

DETERMINATION OF HYGROSCOPIC WATER.

Break the sample down quickly to about pea size, mix thoroughly in a large glazed earthenware or metal dish, and weigh out from ½ to 1 kilo. into a copper box about 4½ inches (114 mm.) long, 3¾ inches (95 mm. wide, and 1½ inches (38 mm.) deep, and dry in a water- or air-bath at

100° C. for at least twelve hours, or until it ceases to lose weight. Fig. 89 shows a convenient form of water-bath. The boxes are numbered, and each one is provided with a counterpoise stamped with the same number as the box, to facilitate the weighing. When a supply of water is not available to run the constant level shown in Fig. 89, the device, on the principle of Mariotte's flask, as shown in Fig. 91, page 252, may be used. The position of the end *b* of the tube *a* fixes the level of the water in the bath.

FIG. 89



A balance sensitive to .1 gramme is sufficiently accurate for weighing these samples. The loss of weight in grammes divided by 5, when ½ kilo. of ore was originally used, gives the percentage of hygroscopic water in the sample. Grind the dried sample very fine, mix it well, heat as much of it as may be required for the analysis in the water-bath, and put it while still hot into a perfectly dry, glass-stoppered bottle.

DETERMINATION OF TOTAL IRON.

Very few iron ores are completely decomposed by hydrochloric acid, the insoluble residue usually containing more or less iron, as silicate, titaniferous iron, etc. The disregard of this fact may occasion grave errors in the determination of iron, and, unless a previous examination has shown the absence of iron in the insoluble residue, it is best to proceed as follows: Place 1 gramme of the finely ground sample in a 150 c.c. beaker, add 10 c.c. hydrochloric acid, and digest it on the hot plate until the residue appears quite white and flotant, or until the acid appears to have no further action. When the ore contains carbonaceous matter, add a little potassium chlorate. Wash off the watch-glass with a fine jet of water, remove it, and evaporate to dryness in the air-bath. Redissolve in about 5 c.c. hydrochloric acid, dilute with 10 c.c. water, allow to settle, and decant the clear liquid into a flask of from 50 to 75 c.c. capacity. Transfer the residue to a small filter, fitted in a funnel placed in the neck of the flask, with as little water as possible, and wash with cold water from a fine jet. Transfer the filter to a small platinum crucible, burn it off, allow the crucible to cool, and pour on the residue 20 or 30 drops of sulphuric acid and about twice as much hydrofluoric acid. Heat carefully, and, if the residue is dissolved, evaporate off the hydrofluoric acid, allow the liquid to cool, and dilute slightly, when it will be ready to add to the solution in the flask, which will have been deoxidized in the meantime by one of the methods explained farther on.

Occasionally this treatment fails to decompose the insoluble residue, in which case heat the crucible until the greater part of the sulphuric acid is driven off; then add about .5 gramme potassium bisulphate, and heat gradually until the potassium bisulphate is quite liquid and fumes of sulphuric acid are given off whenever the lid of the crucible is raised. When all the black specks have disappeared, allow the crucible to cool, and dissolve the salt in the crucible with hot water and a few drops of hydrochloric acid.

Several methods are used for the deoxidation of the solution of ferric chloride, but the one in general use is by adding metallic zinc to the solution. The iron is deoxidized according to the reaction $Fe_2Cl_6 + Zn = 2FeCl_2 + ZnCl_2$, while the excess of hydrochloric acid is decomposed and hydrogen liberated, $2HCl + Zn = ZnCl_2 + 2H$. As all zinc contains a small amount of iron, the amount added to the solution should be roughly weighed. Add

then to the solution in a flask 3 grammes of granulated zinc, and, when the evolution of hydrogen has somewhat slackened, heat the flask slightly. The neck of the flask is closed by a small funnel, which allows the hydrogen to escape while the liquid is caught on the funnel and falls back into the flask. It sometimes happens as the solution becomes neutralized that a basic salt of ferric oxide is thrown down, giving the solution a reddish color; in this case add a few drops of hydrochloric acid, and when the solution finally becomes colorless add a few drops more of hydrochloric acid. If this fails to produce a yellowish coloration, the solution may be considered deoxidized. Pour in through the funnel the solution of the residue insoluble in hydrochloric acid, and add gradually a mixture of 10 c.c. sulphuric acid and 20 c.c. water. This addition of sulphuric acid is a very necessary part of the operation, for it not only serves to dissolve the remainder of the zinc which is unacted on when the deoxidation is complete, but it supplies the proper amount of zinc sulphate, which makes the end reaction with potassium permanganate as sharp as if no hydrochloric acid were present in the solution. As soon as all the zinc is dissolved, wash down the funnel inside and out and the neck of the flask with a fine jet of water, filling the flask almost full, cool the flask in water, and when the solution is quite cold transfer it to a large white dish of about 1500 c.c. capacity. Wash the flask and funnel well with cold water, pour the rinsing into the dish, and make the solution up to about 1000 c.c. Run in from a burette a standard solution of potassium permanganate (Marguerite's method), the value of which has been carefully determined by one of the methods described farther on. At first the color of the permanganate is destroyed almost as soon as it touches the liquid in the dish, which should be stirred carefully with a glass rod. The permanganate should be added more and more slowly until towards the end of the operation it is added only drop by drop. The liquid in the dish gradually assumes a yellowish tint, which is deeper the larger the amount of iron in the ore. Finally a drop of the permanganate seems to destroy the yellow color, and the next drop gives the liquid a very faint pink tinge. This is the end of the reaction. Take the reading of the burette, and then add another drop, which will cause the solution to become decidedly pink in color. The number of c.c. of the standard solution used when the reading was taken, less a small correction for the zinc, etc., noted farther on, multiplied by the value of 1 c.c., gives the amount of metallic iron in the ore.

The simple form of reductor (Fig. 49) shown on page 89 may be used for deoxidizing the solution of the ore in which the iron is in the form of sulphate. With amalgamated zinc it is a most excellent and rapid device. The method of reduction is given on page 90 in the description of the method of standardizing the potassium permanganate solution.

When using a standard solution of potassium bichromate (Penny's method), the end reaction is not rendered apparent by a change in the color of the solution, but the presence or absence of ferrous salt in the solution is determined by taking a drop from the dish on the end of the stirring-rod and allowing it to run into a drop of a dilute, freshly made solution of potassium ferricyanide placed on a white tile or capsule. Dissolve a very small crystal of potassium ferricyanide in a few c.c. of water, and place a number of drops of the solution on a white tile or on a flat-bottomed capsule. Run the carefully standardized solution of potassium bichromate from the burette into the deoxidized iron solution previously placed in a white dish. The solution, at first colorless, changes gradually to a decided chrome-green from the reduction of the chromic acid. Test the progress of the oxidation of the iron solution by transferring a drop of it on the end of the stirring-rod to one of the drops of ferricyanide. As the blue color produced becomes less intense, add the bichromate more slowly and make the test more frequently, towards the end of the operation after the addition of each drop of bichromate. When, finally, no color appears in the test-drops, even after the lapse of several moments, the oxidation of the ferrous salt is complete, and the amount of bichromate used, less a small correction for the zinc, is the measure of the amount of iron in the ore. The potassium ferricyanide employed must, of course, be perfectly free from ferrocyanide: it may be tested by adding a drop of ferric chloride solution to one of the drops of ferricyanide solution, the absence of any resulting blue color in the test-drops being proof of the purity of the ferricyanide. As towards the end of the operation the frequent tests become rather tedious, some analysts prefer to make the determinations in duplicate, using the first to get an approximate result.

When the ore is completely decomposed by hydrochloric acid, a separate treatment of the residue is unnecessary, and the ore may be weighed at once into the flask and treated with 10 c.c. hydrochloric acid and a little potassium

chlorate when organic matter is present. When the ore is completely decomposed, and any chlorine from the potassium chlorate driven off, add 30 c.c. of water, and proceed with the deoxidation.

Instead of deoxidizing the solution of ferric chloride by zinc, it may be deoxidized by a solution of ammonium bisulphite. In fact, the deoxidation by zinc is not practicable in ores containing much titanic acid, for the titanic acid is reduced by metallic zinc to titanic oxide, imparting a purple or blue color to the solution, and acting like a solution of ferrous salt on the standard solution of permanganate. In deoxidizing a solution of ferric chloride by this method it should be placed in a flask of 120 c.c. capacity, and two or three small spirals of platinum wire added to facilitate the subsequent boiling. Add cautiously to the solution (which should not exceed 40 c.c. in volume) enough ammonia to produce a slight permanent precipitate of ferric hydrate, which remains even after vigorous shaking. Add now 5 c.c. of a strong solution of ammonium bisulphite,* shake vigorously, and warm the flask gently. As the color of the solution (at first a deep red) fades, increase the heat, and finally heat to boiling. When the solution is colorless, add to it the solution of the residue and 10 c.c. sulphuric acid mixed with 20 c.c. water. Boil the solution until all the sulphurous acid is driven off. When the escaping steam no longer smells of sulphurous anhydride, place the flask in cold water, wash down the funnel and the neck of the flask, filling the latter full of water, and when the solution is cold transfer it to a dish and titrate with a standard solution.

A third method of deoxidizing the solution of ferric chloride is used, in which the reducing agent is a solution of stannous chloride. The investigations of Zimmermann † and Reinhardt ‡ have made this method of reduction a favorite one, especially when, by the use of phosphoric acid and manganous sulphate, the subsequent titration with potassium permanganate is practicable. The details are as follows. Prepare the following solutions:

1. Phosphoric acid solution. Dissolve 200 grammes of crystallized manganous sulphate in 1 litre of water, add a few drops of sulphuric acid, and filter. Add to this 1 litre of phosphoric acid (1.3 sp. gr.), 600 c.c. water, and 400 c.c. strong sulphuric acid.

2. Stannous chloride solution. Dissolve 120 grammes of granulated

* See page 39.

† Berichte d. Chem. Ges., 1884, xv. 779.

‡ Chem. Zeit., xiii. 324.

tin, free from iron, in 500 c.c. hydrochloric acid (1.19 sp. gr.), dilute to 1 litre, and filter through asbestos. To the filtrate add 1 litre of hydrochloric acid (1.124 sp. gr.) and 2 litres of water.

3. Mercuric chloride solution. Dissolve 50 grammes of mercuric chloride in 1 litre of water and filter.

Dissolve 1 gramme of the ore in 30 c.c. strong hydrochloric acid (if necessary, ignite, and fuse the residue with a little sodium carbonate, dissolve in water and hydrochloric acid, and add to the main solution), transfer to a 150 c.c. Erlenmeyer flask, heat to boiling, and add, from a burette stannous chloride solution until the color of the solution fades completely. Pour into the dish 600 c.c. of water and add to it 60 c.c. of the phosphoric acid solution. To the deoxidized solution in the flask add 60 c.c. of the mercuric chloride solution, pouring it all in at once, shake vigorously and wash the solution out into the dish, using plenty of wash-water, and titrate with permanganate in the usual way. The phosphoric acid makes the solution nearly colorless by forming ferric phosphate, and the end reaction is very sharp.

The mercuric chloride should not be added until everything is ready for the titration, as the absence of any deoxidizing substance may cause the solution to become slightly oxidized on standing.

Mixer and Dubois* give several modifications of the method as used in the Lake Superior region. They employ a solution of potassium permanganate of such strength that 1 c.c. equals 2 per cent. of iron when .5 gramme of ore is used. They use for standardizing the permanganate an iron ore the amount of iron in which is accurately known, and if the permanganate is not exactly of the proper strength, such a weight of the ore is taken, approximately .5 gramme, that the reading of the burette multiplied by 2 gives the percentage of iron. Necessarily this implies the use of the same weight of the ore to be analyzed. They also add to the ore about 2.5 c.c. of 25 per cent. solution of stannous chloride before adding the hydrochloric acid, as this is said to very much hasten the solution of the ore.

Methods for Standardizing the Solutions.

It is of the utmost importance that the value of the standard solution employed should be determined with the greatest accuracy if the results obtained by its use are to be anything but mere approximations.

* Journal of the American Chem. Soc., xvii. 405.

The best method for standardizing solutions of potassium permanganate is by the use of sodium oxalate exactly as described on page 90, using .5 and .55 gramme sodium oxalate which will take about 58.8 c.c. and 68.7 c.c. permanganate solution.

$$Na_2C_2O_4 + H_2SO_4 = Na_2SO_4 + H_2C_2O_4$$
$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = 2MNSO_4 + 10CO_2 + 8H_2O.$$

When using ferrous sulphate the reaction is $10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$, so that one molecule of sodium oxalate is equal in reducing power to two molecules of ferrous iron and the factor for the ratio of sodium oxalate to iron is 0.8334.

Sodium oxalate cannot be used to standardize potassium bichromate, so that ferrous sulphate, ferrous ammonium sulphate or iron wire must be used for this purpose.

Ferrous sulphate, $FeSO_4,7H_2O$,* containing 20.0082 per cent. iron, or the ferrous-ammonium sulphate, $FeSO_4,(NH_4)_2SO_4,6H_2O$,† containing 14.2400 per cent., may be used to determine the value of the standard solutions. The pure salts are generally weighed, dissolved in water with 10 c.c. sulphuric acid added, and titrated direct, but they are not so satisfactory in use as the first methods described. It is important to have the standard solutions of the proper strength,—that is, neither too dilute nor too concentrated for convenience in working. As iron ores rarely contain more than 60 per cent. metallic iron, a standard solution 100 c.c. of which are equal to .70 gramme iron will be found sufficiently concentrated to avoid the necessity of refilling the burette for a determination; and where ores much poorer than this are habitually used the solutions may be correspondingly more dilute.

In the case of potassium bichromate the raction is $6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 = 3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$. For ores high in iron 4 grammes of potassium permanganate or 6 grammes of potassium bichromate to the litre give solutions of the proper strength.

To prepare the solutions, therefore, dissolve the above weights, or multiples of them, in pure distilled water, allow the solution to stand for some little time, filter through asbestos or the alundum plate, and dilute to the proper volume. Mix thoroughly by shaking in the bottle, and standardize

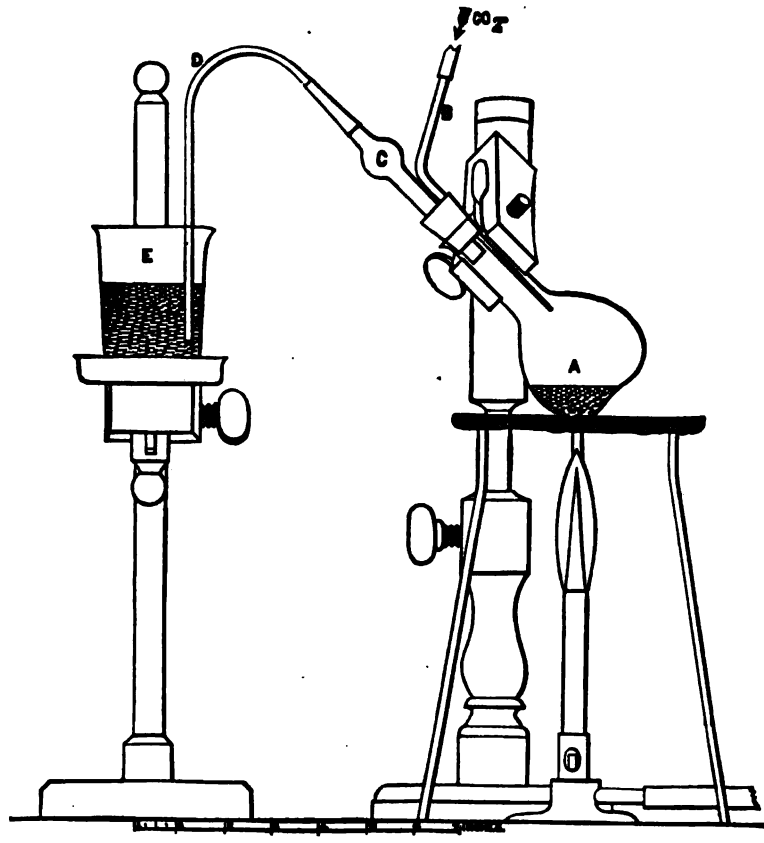
* See page 51. † See page 51.

as above directed. The solutions should be kept in glass-stoppered bottles in a dark closet, and the bottles should be well shaken whenever the solution is used.

DETERMINATION OF IRON EXISTING AS FERROUS OXIDE.

Many iron ores contain iron in the state of ferrous oxide, and this may be either soluble or insoluble in hydrochloric acid. To determine

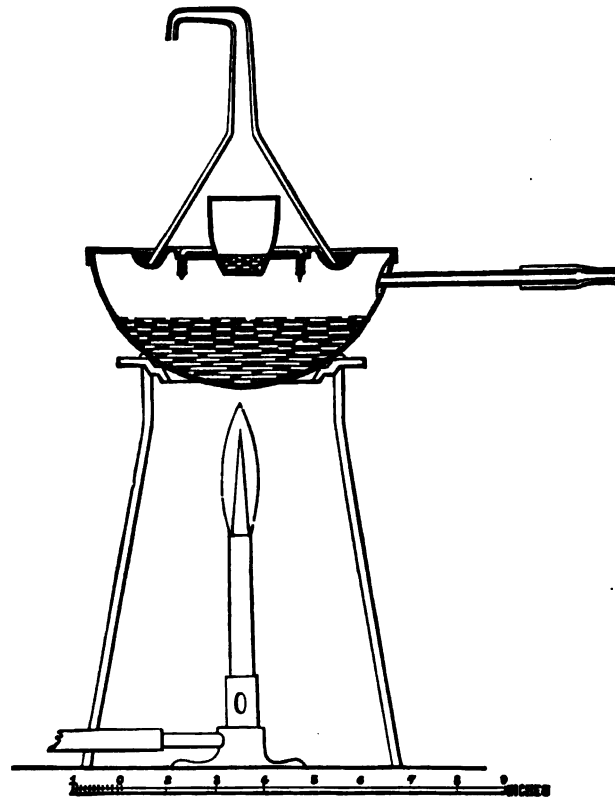
FIG. 90



the ferrous oxide soluble in hydrochloric acid, place 1 gramme of the finely ground ore in the flask A, Fig. 90, of about 100 c.c. capacity. Close the flask with a rubber stopper fitted with the two glass tubes B and C, and

place it in the position shown in the sketch. Connect the tube C by means of a piece of rubber tubing with the bent tube D dipping below the surface of the water in the beaker E. Pass a current of carbonic acid through the tube B until all the air is expelled, then remove for a moment the rubber tube connecting B with the source of carbonic acid, and by means of a small funnel and rubber tube introduce into the flask A,

FIG. 91



through B, from 10 to 12 c.c. strong hydrochloric acid, and establish the current of carbonic acid as before. Heat the flask carefully, and when the ore is entirely decomposed, or the hydrochloric acid ceases to exert any further action on it, remove the source of heat, stop the current of carbonic acid for the moment, cool the flask with the hand, and allow the partial vacuum thus formed to draw the water from E back into A. Turn on the

current of carbonic acid again, place a dish of cold water under the flask A, and allow the solution to cool. Dissolve in a small flask 3 grammes of metallic zinc in 10 or 15 c.c. sulphuric acid, diluted with the proper quantity of water, cool it, and have it ready to pour into the titrating-dish by the time the solution in the flask A is cool. Wash the solution of the ore from the flask A into the dish, add the zinc solution, dilute to 1 litre, and titrate with a standard solution. Subtract from the burette reading the proper correction, calculate the percentage of iron, divide by 7, and multiply by 9. The result is the percentage of ferrous oxide in the ore soluble in hydrochloric acid. Allow the solution in the dish to stand for a few minutes, when all the undecomposed particles of ore will settle. Draw off the greater part of the clear supernatant fluid with a siphon, wash the sediment into a beaker with a jet of cold water, filter on a thin felt* in a Gooch crucible, and wash the sediment on the felt with cold water. Transfer the felt and sediment to a platinum crucible, pour into the crucible from 5 to 10 c.c. of hydrochloric acid and about half the quantity of hydrofluoric acid, cover the crucible, and place it in the water-bath shown in Fig. 91. The crucible rests on a platinum triangle fixed over the hole in the centre of the top of the bath. Around this hole is a groove in which a funnel stands as shown in the cut, while the water in the groove forms a tight joint.† Pass a current of carbonic acid or coal-gas through the tube in the side of the bath, as figured in the cut, to exclude the air, and heat the bath until the residue and felt are completely dissolved. Wash the crucible out into the titrating-dish into which have been poured just previously 3 grammes of zinc dissolved in sulphuric acid and enough cold water to make the solution up to nearly 1 litre. Titrate, and calculate the amount of ferrous oxide as before.

Of course separate portions of the ore may be used to determine the ferrous oxide soluble and insoluble in hydrochloric acid, but it is more troublesome, and experience has shown that it is no more accurate, and in some cases less accurate, than the method just described.

The total ferrous oxide may also be determined in one operation by

* The asbestos of which the felt is made must be free from ferrous oxide.

† Avery, Chem. News, xix. 270; Wilbur and Whittlesay, Crook's Select Methods, p. 133.

treating 1 gramme of the ore direct in the crucible with 20 c.c. hydrochloric acid and 20 c.c. hydrofluoric acid, but it is often difficult to get the ore perfectly dissolved even by prolonged heating in the bath, and the ore must be ground very fine in the agate mortar. It is necessary to remove the funnel from time to time, raise the lid of the crucible, and stir the contents with a platinum wire.

When the ore is completely decomposed by hydrochloric acid, or when the portion undecomposed contains no ferrous oxide, the treatment of the residue is unnecessary.

When an ore contains much organic matter, an accurate determination of ferrous oxide is often impossible, as the solution of the ore in hydrochloric acid reduces some of the ferric salt.

DETERMINATION OF SULPHUR.

Sulphur exists in two conditions in iron ores, as sulphur in the form of sulphides and as sulphuric acid in the form of sulphates. To determine the total sulphur, place 1 gramme of the finely ground ore in a large platinum crucible, add to it 10 grammes of sodium carbonate and a little potassium nitrate (less than 1 gramme *). Mix thoroughly with a platinum wire, and heat carefully over a large alcohol lamp until the mass appears perfectly liquid and in a tranquil state of fusion. Run the fusion well up on the sides of the crucible, allow it to cool, and treat it in the crucible with boiling water. Pour the liquid into a tall, narrow beaker, treat the crucible again with boiling water, and repeat the operation until all the sodium salts are dissolved and nothing remains in the crucible except the unavoidable stains. Stir the liquid in the beaker well and allow the iron oxide to settle. If the solution is colored red or green, it is proof of the presence of manganese in the ore; add a few drops of alcohol, which will precipitate the manganese as oxide, leaving the solution colorless unless the ore contains chromium, in which case the solution will be yellowish. Decant the supernatant liquid on a small filter, allowing the filtrate to run into a 600 c.c. beaker, fill the small beaker nearly full of

* It is well to make a blank determination, using the same amounts of sodium carbonate, potassium nitrate, and hydrochloric acid, applying the amount of barium sulphate found as a correction.

hot water, stir well, and allow to settle. Decant again on the filter, and repeat the operation once more. Acidulate the collected filtrates with hydrochloric acid (about 20 c.c. will be required), evaporate to dryness in the air-bath, redissolve in water with a few drops of hydrochloric acid, filter into a 400 c.c. beaker, heat the filtrate to boiling, and add 10 c.c. of a boiling solution of barium chloride. Allow to stand for some hours, filter on a Gooch crucible or on a small ashless filter, ignite, and weigh as barium sulphate, which multiplied by .13734 gives the weight of sulphur. The insoluble portion from the aqueous solution of the fusion may be used to determine the total iron in the ore, and is very convenient for this purpose in ores difficult to dissolve. Pour into the crucible in which the fusion was made about 10 c.c. of hydrochloric acid, place the lid on the crucible, and warm slightly to dissolve the adhering oxides, dilute with an equal bulk of water, and pour it on the small filter through which the aqueous solution was decanted, allowing it to run into the beaker which contains the residue of iron oxide, etc. Wash out the crucible, pouring the washings on the filter, and wash the filter free from ferric chloride with a jet of cold water. Evaporate the solution in the beaker to dryness, redissolve in 10 c.c. hydrochloric acid, and transfer the solution of ferric chloride, the silica, etc., to one of the small flasks, deoxidize, and titrate as directed.

The sulphur which exists as sulphuric acid in an iron ore is usually combined with either calcium or barium: as calcium sulphate or of any of the other alkaline earths except barium, of the alkalies, or of the metals, it is soluble in hydrochloric acid; as barium sulphate it is practically insoluble. We may, therefore, determine the soluble sulphates as follows. Boil 10 grammes of the ore with 30 c.c. hydrochloric acid and 60 c.c. water, filter from the mass of the undissolved ore, evaporate the filtrate to dryness, redissolve in hydrochloric acid and water (1 to 2), filter into a 250 c.c. beaker, nearly neutralize by ammonia, heat to boiling, and precipitate by barium chloride solution. Filter and wash the precipitate, ignite and weigh as barium sulphate, which contains 34.297 per cent. sulphuric anhydride.

To determine the sulphuric acid which exists as barium sulphate, treat 10 grammes of the ore with 50 c.c. hydrochloric acid until the ore appears to be decomposed. Evaporate to dryness, redissolve in dilute hydrochloric acid (1 to 3), dilute, filter, and wash the insoluble matter thoroughly. Ignite

and fuse the insoluble matter with sodium carbonate, treat the fused mass with hot water, and filter. In the filtrate is the sulphuric acid as sodium sulphate, while the barium remains on the filter as barium carbonate. It is safer to calculate the barium sulphate from the amount of barium rather than from the amount of sulphuric acid, as the ore may contain sulphides (pyrites, etc.) which are not decomposed by hydrochloric acid, but are decomposed and partly oxidized by fusion with sodium carbonate. The other forms of barium besides the sulphate (silicate and carbonate) are readily decomposed by hydrochloric acid, and are not likely to be found with the barium in the insoluble residue. It is, of course, possible to suppose the coexistence of barium silicate or carbonate and of calcium sulphate in an ore, and the consequent formation of barium sulphate when the ore is decomposed by hydrochloric acid; but, as the soluble sulphuric acid is determined in one operation and the insoluble in another,* the total amount of sulphuric acid existing as such is determined and the object of the analysis attained. To determine the barium, then, treat the insoluble matter obtained by the filtration of the aqueous solution of the fusion by dilute hydrochloric acid, evaporate to dryness to render the silica insoluble, redissolve in water with a few drops of hydrochloric acid, filter into a 250 c.c. beaker, heat the filtrate to boiling, and add a few drops of sulphuric acid diluted with a little water. Allow the precipitate to settle, filter, wash, ignite, and weigh as barium sulphate, from which weight calculate the amount of sulphuric anhydride in the ore insoluble in hydrochloric acid. To find the amount of sulphur existing as sulphides, subtract from the total sulphur the amount of sulphur in the sulphuric anhydride found as sulphates.

DETERMINATION OF PHOSPHORIC ACID.

Acetate Method.

Treat 5 to 10 grammes of the finely ground ore in 30 or 60 c.c. hydrochloric acid. (With low phosphorus ores use 10 grammes; with others, 5 grammes.) When the ore is decomposed, evaporate to dryness, redissolve

* The insoluble matter from the treatment of 10 grammes of the ore with hydrochloric acid for the determination of soluble sulphates (page 255) may be used to determine the barium sulphate.

in 20 or 40 c.c. hydrochloric acid, dilute, filter, and proceed exactly as directed in the determination of phosphorus in iron and steel (page 76 *et seq.*). The weight of the magnesium pyrophosphate multiplied by .63793 gives the weight of the phosphoric acid. The weight of the ammonium phospho-molybdate multiplied by .03735 gives the weight of the phosphoric acid.

Molybdate Method.

Treat 2 to 5 grammes of ore as above. Filter off the insoluble matter, evaporate the filtrate to low bulk and replace the hydrochloric acid with nitric acid by evaporating the solution twice nearly to dryness with additions of 15 to 20 c.c. of nitric acid. Ignite the insoluble matter, treat it with hydrofluoric and a few drops of sulphuric acid. Evaporate to dryness and ignite. Fuse the residue with a little sodium bicarbonate, dissolve in water, filter and add the filtrate to the nitric acid solution. Transfer the solution to an Erlenmeyer flask, precipitate and determine the phosphorus as directed on page 92. The phosphorus obtained multiplied by 2.2887 gives the phosphoric anhydride.

Titanic acid is very generally found associated with iron ores, and may be regarded as one of the usual constituents. As mentioned on page 80, its presence, if overlooked, may lead to serious errors in the determination of phosphoric acid. When an ore contains much titanic acid it may readily be recognized by the peculiar milky appearance of the solution when it is diluted preparatory to filtering off the insoluble matter, and by the strong tendency it shows to run through the filter as soon as the attempt is made to wash the insoluble matter with water. Smaller quantities of titanic acid may be recognized by the clouding of the solution when it is deoxidized by ammonium bisulphite, as noted on page 83. In the latter case, however, this clouding may be caused by the formation of barium sulphate when the ore contains the latter element in the form of carbonate or silicate. Under these circumstances silica in the solution may also cause a cloud which closely resembles that of titanic acid, while barium sulphate may readily be distinguished from either by its granular appearance and its tendency to settle to the bottom of the beaker.

The insoluble residue from the solution of the ore in hydrochloric acid

should, therefore, be treated to recover any phosphoric acid which may have remained insoluble in combination with titanic acid.* An additional test for the presence of titanic acid, and one that rarely fails even with very small amounts, is to dissolve the insoluble matter from the aqueous solution of the fusion of the residue from the hydrofluoric acid and sulphuric acid treatment of the insoluble portion of the ore in dilute hydrochloric acid, allowing it to run into a test-tube and adding metallic zinc. When titanic acid is present the solution first becomes colorless, then pink or purple, and finally blue from the formation of titanic oxide. The simplest way is to proceed as directed on pages 82 and 83 when using the acetate method, or on page 87 when using the molybdate method. These methods are not practicable, however, when the ore contains a very large amount of titanic acid, and recourse must be had to the method described on page 80, involving the fusion of the acetate precipitate and the residue from the treatment of the insoluble matter with hydrofluoric and sulphuric acids, with sodium carbonate and a little sodium nitrate. At any rate, it is best to pursue this method whenever titanic acid is also to be determined, as the same portion can be used for the estimation of both titanic acid and phosphoric acid, and the aggregate labor involved is much lessened.

DETERMINATION OF TITANIC ACID.

The determination of titanic acid has always presented many difficulties, and its separation from a large amount of ferric oxide and alumina has been far from satisfactory, besides being most tedious. The principal sources of error in the estimation of titanic acid in iron ores are the tendency of phosphoric acid to prevent the precipitation of titanic acid by boiling when its sulphuric acid solution contains phosphoric acid and ferrous sulphate, and the liability of alumina to separate out with the titanic acid when the latter is precipitated under the circumstances above mentioned. There is also a mechanical difficulty, caused by the adhesion of the precipitated

* When hydrofluoric acid is not available, fuse the residue with sodium carbonate, treat the fused mass with hot water, filter, acidulate the filtrate with hydrochloric acid, and evaporate to dryness to render the silica insoluble. Redissolve in water with a little hydrochloric acid, filter, add a little ferric chloride, and make a separate acetate precipitation in this portion, adding the solution to the solution of the main acetate precipitation.

titanic acid to the bottom and sides of the beaker, from which it can sometimes be removed only by boiling with a strong solution of caustic potash. The admirable series of experiments carried out by Dr. Gooch * on the separation of aluminum and titanium suggests a method which renders the determination of titanic acid in iron ores much less troublesome, while adding greatly to the accuracy of the results. In carrying out the details of the method, dissolve 5 or 10 grammes of the ore in hydrochloric acid, and proceed exactly as in the determination of phosphoric acid, by fusing the residue from the treatment of the insoluble matter by hydrofluoric and sulphuric acids and the acetate precipitate with sodium carbonate and a little sodium nitrate, and then complete the operation exactly as described in the determination of titanium in pig-iron.†

The essential points in this method are: 1. Separation of the titanic acid from the mass of ferric oxide by ammonium acetate in the deoxidized solution. 2. Separation from all the phosphoric acid and the greater part of the alumina by fusion with sodium carbonate, by which means a sodium titanate insoluble in water is formed, and at the same time sodium phosphate and aluminate soluble in that menstruum. 3. Separation of the last traces of alumina from the ferric oxide, lime, etc., by precipitating the titanic acid in the thoroughly deoxidized solution in the presence of a large excess of acetic acid and some sulphurous acid, the sulphuric acid being all in the form of sodium sulphate. The addition of a large excess of sodium acetate, by which this latter condition is effected, converts all the sulphate into acetates, and precipitates the titanic acid almost instantaneously as a hydrate, which is flocculent, settles quickly, shows no tendency to run through the filter, and is washed with the greatest ease. It sometimes happens that a little ferrous oxide is precipitated with the titanic acid, and the latter, after ignition, appears discolored; in this case fuse with a little sodium carbonate, add sulphuric acid to the cold fused mass, dissolve, and repeat the precipitation with sodium acetate in the presence of sulphurous and acetic acids exactly as in the first instance.

A number of experiments covering all the points involved in this method show it to be extremely accurate and entirely trustworthy.

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* Proceedings Am. Acad. Arts and Sciences, New Series xii, 435.

† Page 172.

DETERMINATION OF MANGANESE.

When manganese alone is to be determined in an ore, any one of the methods described under the determination of manganese in iron and steel (page 103) may be used. The most convenient, however, is Ford's method with the modifications necessary in the analysis of pig-iron (page 110). The only change requisite is to evaporate the solution in hydrochloric acid to dryness to render silica insoluble before filtering off the insoluble matter.

In the determination of manganese in high grade manganese ores it is best to use a one-tenth factor weight (0.3873 gramme) of the sample, dissolve in hydrochloric acid, evaporate to dryness, redissolve in dilute hydrochloric acid, and filter off the insoluble matter. Ignite the insoluble matter in a platinum crucible, fuse with a little sodium carbonate, dissolve in water, acidulate with hydrochloric acid, and evaporate to dryness. Redissolve in dilute hydrochloric acid and filter into the main solution. Or, treat the ignited insoluble matter with sulphuric and hydrochloric acids, drive off the hydrofluoric and the excess of sulphuric, cool, add water and a little hydrochloric acid, and heat until the residue dissolves, then add the solution to the main solution of the ore.

Evaporate the main solution until it is syrupy, add an excess of strong nitric acid and evaporate off the hydrochloric acid. Precipitate by potassium chlorate in the usual way and filter through asbestos. Wash the precipitate thoroughly with cold water to get rid of the calcium nitrate, which, being practically insoluble in strong nitric acid, will remain with the precipitated manganese dioxide unless this precaution be observed. There is no danger of dissolving the manganese dioxide by this treatment.

Proceed with the determination as directed on page 108. Each milligramme of manganese pyrophosphate is a tenth part of one per cent. of manganese in the ore.

In using the acetate method it is, of course, necessary that all the iron should be in the form of ferric chloride, and also that there should be no reducing agent in the solution. Even a very small amount of ferrous chloride will cause the formation of a "brick-dust" precipitate, which cannot be kept from passing the filter while some of the iron remains dissolved in the acetate solution. When, therefore, the ore contains ferrous oxide, it should be oxidized by nitric acid or potassium chlorate, and the excess of the oxidizing agent removed by evaporation with hydrochloric acid.

Volhard's Method Applied to High Grade Manganese Ores.

Dissolve 1 gramme of the ore in a small beaker in hydrochloric acid, heat until the chlorine is all driven off, wash out into a platinum dish (Fig. 31), and add 5 c.c. strong sulphuric acid and a little hydrofluoric acid. Evaporate to dryness and heat until the sulphuric acid begins to volatilize. Cool, dissolve in water, transfer to a 300 c.c. flask, and proceed as directed on page 110, except that 100 c.c. of the filtered solution represents one-third if a gramme of the ore is used.

It is necessary to heat the solution in the flask after there appears to be a slight excess of permanganate. This will make the precipitate settle rapidly and generally show the necessity for adding more permanganate.

A large number of comparative analyses have shown that it is necessary to add one one-hundredth of the amount obtained to get the true percentage of manganese; in other words, the results obtained are always one one-hundredth too low.

For instance, if by calculation the ore contains 50 per cent. of manganese by this method, the true result is 50.5 per cent.

The Fusion Method.

The best method for the determination of manganese in manganese ores is that described on page 118.

DETERMINATION OF MANGANESE DIOXIDE.

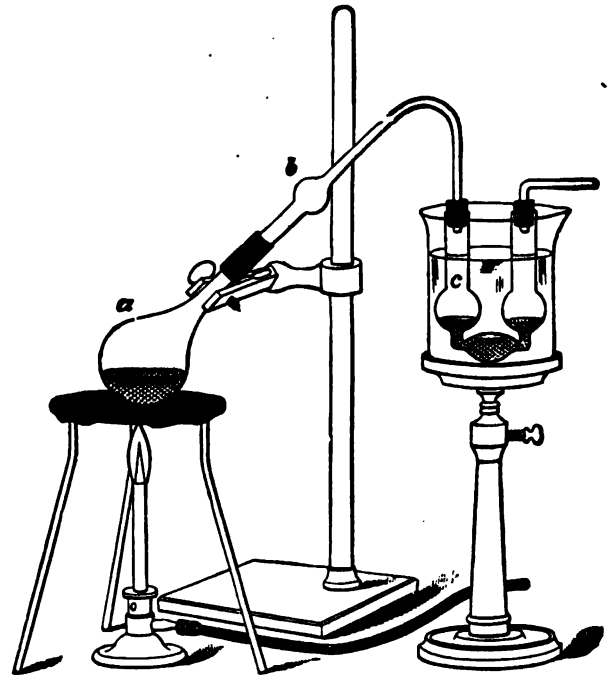
Many manganiferous iron ores contain manganese in a higher state of oxidation than the protoxide, and the determination of the excess of oxygen is often necessary. All ores of this character when treated with hydrochloric acid evolve chlorine gas, which is easily recognized by its yellowish-green color and peculiarly irritating odor. The reaction by which chlorine is liberated is $MnO_2 + 4HCl = MnCl_2 + 2H_2O + 2Cl$, or each molecule of manganese dioxide = 86.93 corresponds to 2 molecules of chlorine = 70.92. This reaction is the basis of Bunsen's method for the estimation of the amount of manganese dioxide in manganese ores, which consists in driving the liberated chlorine into a solution of potassium iodide, and determining the amount of iodine set free by starch and hyposulphite

solution. When the method given on page 63 for determining sulphur in steel is in use, the solutions employed in carrying out that method (with the exception of the iodine in potassium iodide) can be used in this, or they may be prepared by the directions there given, for use in this method.

Bunsen's Method.

Weigh from .5 gramme to 1 gramme of the finely ground ore and place it in the flask *a*, Fig. 92, pour in 10 c.c. strong hydrochloric acid, connect

FIG. 92



the bent tube *b* quickly by means of a piece of rubber tubing, and heat the flask gently at first and finally to boiling to drive all the chlorine over into the tube *c*, which contains a strong solution of pure potassium iodide free from iodate. This tube is placed in ice-water. When all the chlorine has been expelled from the flask *a* and absorbed in *c*, detach the latter, wash its

contents into a large dish, add a little starch solution, and run in the hyposulphite until the blue color just vanishes. If, as in the example given on page 66, 1 c.c. of the hyposulphite solution is equal to .01267 gramme of iodine, and 1 equivalent of chlorine = 35.45 replaces 1 equivalent of iodine = 126.97 in the potassium iodide, 1 c.c. of the hyposulphite solution would be equal to (126.97 : 35.45 :: .01267 : .003537) .003537 gramme of chlorine; and, as 1 equivalent of manganese dioxide = 87 is equal to 2 equivalents of chlorine = 70.90, 1 c.c. of the hyposulphite solution would be equal to (126.97 : 35.45 :: .01267 : .003537) .003537 gramme of chlorine; and, as 1 equivalent of manganese dioxide = 87 is equal to 2 equivalents of chlorine = 70.90, 1 c.c. of the hyposulphite would be equal to (70.90 : 87 :: .003537 : .004341) .004341 gramme manganese dioxide.

DETERMINATION BY SODIUM OXALATE.

Place .5 gramme of the very finely ground ore and .75 gramme of sodium oxalate in a 500 c.c. Erlenmeyer flask, add 100 c.c. of dilute sulphuric acid, 1 part of acid to 5 of water, cover with a watch glass and boil until the ore is decomposed. This may take from ten to twenty minutes. Dilute with hot water to 300 c.c. and titrate the excess of oxalate with permanganate solution, 4 grammes to the litre. Standardize the permanganate solution, using .75 gramme of sodium oxalate, and find the value of 1 c.c. of the permanganate. Subtract the number of c.c. of the permanganate corresponding to the excess of oxalate in the titration of the ore from the number found equivalent to .75 oxalate, and the difference is the value of the oxalate oxidized by the ore in the permanganate.

Then $Na_2C_2O_4 : MnO_2 = 1 : 64873$ and the number of c.c. of the permanganate multiplied by the value of 1 c.c. in oxalate and the result by .64873 gives the amount of MnO_2 and this multiplied by 2 gives the amount in 1 gramme of the ore, which divided by 100 gives the per cent. of MnO_2 in the ore.

Then as $Na_2C_2O_4 : O = 1 : 1194$, substitute 0.1194 for 0.64873 in the above calculation and the result is the available oxygen in the ore.

DETERMINATION OF SILICA, ALUMINA, LIME, MAGNESIA, MANGANESE OXIDE, AND BARYTA.

Treatment of iron ores with hydrochloric acid leaves a residue which only in very rare instances consists of silica alone, being usually silicates of aluminum, calcium, and magnesium, mixed with an excess of silica. These silicates are often much more complicated, and contain, besides the substances enumerated above, ferrous oxide, soda, potash, and manganese oxide. With these silicates are occasionally found titanic acid, titaniferous iron, chrome irone ore, barium sulphate, and ferrous sulphide, besides organic matter, and sometimes graphite. As this residue must be fused with sodium carbonate in order to decompose it, and the introduction of sodium salts into the main solution is not desirable, the two portions of the ore (the soluble and the insoluble in hydrochloric acid) should be analyzed separately.

Place 1 gramme of ore in a 150 c.c. beaker, add 15 c.c. hydrochloric acid, cover with a watch-glass, and digest at a gentle heat until the ore appears to be quite decomposed, add a few drops of nitric acid, heat until the action has ceased, and then wash off the cover with a fine jet of water and evaporate to dryness. Redissolve in hydrochloric acid, and evaporate to dryness a second time to render all the silica insoluble. Redissolve in 10 c.c. hydrochloric acid and 30 c.c. water, filter, transfer all the residue to the filter (a small ashless filter) with a fine jet of cold water, using a "policeman" to detach any adhering particles from the beaker, and wash the filter with a little hydrochloric acid and plenty of cold water. Allow the filtrate and washings to run into an 800 c.c. beaker, and ignite and weigh the residue as "Insoluble Silicious Matter."

Add to the insoluble matter in the crucible about ten times its weight of pure dry sodium carbonate and fuse it. Run the fusion well up on the sides of the crucible, cool, and dissolve in hot water. Transfer to a platinum dish, dissolve any particles adhering to the crucible in hydrochloric acid, and add this to the solution in the dish. Acidulate with hydrochloric acid, evaporate to dryness, moisten with hydrochloric acid and water, evaporate to dryness a second time to render silica insoluble, then pour into the dish 5 c.c. hydrochloric acid and 15 c.c. water, and stand it in a warm place for some time. Dilute with about 20 c.c. water, filter on a small ashless filter, wash well with hot water, receiving the filtrate and washings in a small beaker,

dry, ignite, and weigh. Treat the ignited precipitate with hydrofluoric acid and a drop or two of sulphuric acid, evaporate to dryness, ignite, and weigh again. The difference between the two weights is silica. If the difference between the last weight and the weight of the empty crucible is more than a milligramme or two, the residue must be examined and its nature determined. This residue may consist of titanic acid, barium sulphate, alumina, or sodium sulphate (from imperfect washing of the silica). If it is titanic acid or alumina, the weight must be added to the weights of the alumina, etc.

Return the filtrate from the silica to the dish in which it was previously contained, heat to boiling, add a few drops of bromine-water and an excess of ammonia, boil until it smells but faintly of ammonia, filter on a small ashless filter, wash well with hot water, dry, ignite, and weigh as alumina, etc. Besides alumina this precipitate may contain titanic acid, chromium sesquioxide, ferric oxide, manganous oxide, and phosphoric acid.

Return the filtrate from this precipitate to the dish, evaporate down to about 100 c.c., add ammonium oxalate and ammonia, boil for a few minutes, allow the precipitate to settle, filter on a small ashless filter, ignite finally for five minutes over a blast-lamp, and weigh as lime. To the filtrate from the lime add microcosmic salt and about one-third the volume of the solution of ammonia, cool in ice-water, stir vigorously several times, and allow to stand overnight so that the precipitated ammonium-magnesium orthophosphate may settle properly, filter, wash with water containing one-third its volume of ammonia and about 100 grammes of ammonium nitrate to the litre, ignite carefully, and weigh. Dissolve the precipitate in the crucible in a little water containing from 5 to 10 drops hydrochloric acid, filter through a small ashless filter, which dry, ignite, and weigh. The difference between the two weights is magnesium pyrophosphate, which, multiplied by .36207, gives the weight of magnesia.

When barium has been shown to exist in the ore, as noted on page 255, heat the filtrate from the "Insoluble Silicious Matter" to boiling, add a few drops of sulphuric acid, boil for a few minutes to allow the precipitate to settle, filter on a small ashless filter, allowing the filtrate and washings to run into an 800 c.c. beaker, dry, ignite, and weigh as barium sulphate, which, multiplied by .65703, gives the weight of barium oxide.

To the cold filtrate from the barium sulphate add ammonia until the

solution is nearly neutralized, then add a solution of ammonium carbonate until a slight permanent precipitate is formed which fails to dissolve after vigorous stirring, and redissolve this by the careful addition of hydrochloric acid, drop by drop, stirring well, and allowing the solution to stand for a short time after each addition of hydrochloric acid. As soon as the solution clears, add a solution of ammonium acetate, made by slightly acidulating 5 c.c. of ammonia by acetic acid, dilute to about 600 c.c. with boiling water, and boil for a few minutes. Allow the precipitate to settle, decant the clear liquid through a large washed filter, pour the precipitate on the filter, and wash it two or three times with boiling water. With the aid of platinum spatula return the precipitate to the beaker in which the precipitation was made, dissolving any portion remaining on the filter or adhering to the spatula in dilute hydrochloric acid, allowing the acid to run into the beaker containing the precipitate. Wash the filter thoroughly with cold water, and evaporate the solution and washings to dryness. Redissolve in dilute hydrochloric acid, filter into a large platinum dish, dilute with hot water,* heat to boiling, and add a slight excess of ammonia. Boil for a few minutes to make the precipitate granular and expel the excess of ammonia, and filter on an ashless filter (using the filter-pump and cone, page 24, with very slight pressure, if practicable). Dissolve any particles of the precipitate adhering to the dish in a very few drops of hydrochloric acid, heating the bottom of the dish slightly, wash off the rod and cover, and wash down the sides of the dish with hot water, add a slight excess of ammonia, heat gently until the precipitate of ferric hydrate separates, wash this onto the filter, and wash the precipitate thoroughly with hot water. Dry the filter and precipitate carefully, transfer the latter to a weighed crucible, burn the filter in a wire, add the ash to the precipitate, and heat the crucible, keeping it carefully covered, and raising the heat very gradually to expel the last traces of moisture from the precipitate of ferric hydrate. Finally heat the crucible to bright redness, and then to the highest temperature of the blast-lamp for from five to ten

* The distilled water used in the complete analysis of iron ores should never be heated in glass vessels for any length of time, as glass is sensibly attacked by it. An experiment in which distilled water free from residue was heated for twelve hours in a Bohemian flask showed that the water dissolved 52 milligrammes of solid matter to the litre, of which 26 milligrammes were silica. The water should always be heated in platinum or porcelain dishes, or in tin-lined copper flasks. For convenience, the water may be poured into the washing-flasks for immediate use.

minutes. Cool, ignite, and weigh as ferric oxide + alumina + phosphoric acid (+ titanic acid + chromic oxide + arsenic acid).

Add the filtrate and washings from the acetate precipitation to those from the precipitation by ammonia, evaporate down to about 200 c.c. in a platinum dish, filter off any slight precipitate of ferric oxide (which must be ignited, weighed, and the weight added to that of the ferric oxide, etc.), add from 20 to 30 drops of acetic acid, heat to boiling, and pass a current of hydrogen sulphide through the solution for fifteen or twenty minutes, keeping the solution hot during the passage of the gas. Filter off the precipitated copper, zinc, nickel, and cobalt sulphides, wash with hydrogen sulphide water containing a little free acetic acid, and to the filtrate add excess of ammonia and ammonium sulphide. Allow the precipitated manganese sulphide to settle, decant the clear, supernatant liquid through a filter, but before pouring the precipitate on the filter remove the beaker containing the filtrate and substitute a clean beaker, as the precipitate is almost certain at first to run through the filter. Wash the precipitate and filter with water containing a little ammonium sulphide, add the clear filtrate and washings together, and stand them aside. Dissolve the precipitate of manganese sulphide on the filter in dilute hydrochloric acid, and wash the filter thoroughly with hot water, receiving the solution and washings in a small beaker. Heat to boiling to expel hydrogen sulphide, and, when the excess is driven off, destroy the last traces with a little bromine-water, transfer the solution to a platinum dish, and precipitate by microcosmic salt and ammonia as directed on page 106. Filter, wash, ignite, and weigh as manganese pyrophosphate, which, multiplied by .4996, gives the weight of manganese oxide.

Acidulate the filtrate from the manganese sulphide with hydrochloric acid, boil off all the hydrogen sulphide, filter from the sulphur deposited by this operation into a platinum dish, add an excess of ammonia and ammonium oxalate, filter, ignite, and heat at the highest temperature of the blast-lamp for fifteen minutes, cool, and weigh as lime.

Precipitate the magnesia in the filtrate as directed on page 106, and determine the weight of magnesium pyrophosphate, which, multiplied by .36207, gives the weight of magnesia.

By adding the elements determined in the insoluble portion to the similar ones in the soluble portion, we get the total amounts of each in the ore.

Thus, we have from the above analysis silica, ferric oxide + alumina + phosphoric acid + chromic oxide + titanic acid + arsenic acid, manganese oxide, lime, and magnesia, and it becomes, of course, necessary to calculate properly the iron in its different states of oxidation and to determine the amount of alumina in the ore. It is much more accurate to determine in separate portions of the ore the amounts of phosphoric acid, arsenic acid, chromic oxide, ferric oxide, and titanic acid than to attempt to make the separation in the precipitate obtained in this portion. Therefore, knowing the amounts of these substances, the ferric oxide from the volumetric determination of iron, as previously described, and the amount of each of the others as found by one of the methods given, add together the weights of the ferric oxide, the phosphoric acid, the chromic oxide, the titanic acid, and the arsenic acid in one gramme of the ore, and subtract the sum from the weight of the precipitate obtained in the above analysis, the result is the weight of alumina in one gramme of the ore.

Iron may exist in an ore in several conditions, as Fe_2O_3, as FeO, as FeS_2, as $FeAs_2$, etc. While it may not always be possible to determine the exact conditions in which it exists, the rule usually followed is, after subtracting from the sulphur existing as sulphides (page 254) the amount necessary to form copper sulphide, nickel sulphide, etc., to calculate the remainder as FeS_2 by multiplying the weight of sulphur by 1.87087. The weight of sulphur subtracted from this gives the weight of iron in the FeS_2. Now from the weight of $FeAs_2$ subtract the weight of arsenic, and the result is the weight of iron existing as iron in the $FeAs_2$.* Add the iron in the FeS_2 to the iron in the $FeAs_2$, and subtract this weight from the iron found as ferrous oxide, the remainder calculated to ferrous oxide is the amount of ferrous oxide in the ore. Subtract the total amount of iron found originally by titration to exist as ferrous oxide from the total iron found in the ore, and calculate the remainder to ferric oxide.

When an iron ore contains only a very small amount of manganese, the acetate separation may be omitted in the method as given above, which simplifies and shortens the operation very materially. In this event transfer the filtrate from the insoluble silicious matter at once to a large platinum dish, heat to boiling, add a few c.c. of bromine-water and then excess of ammonia,

* All the weights, of course, are calculated to one gramme of ore.

boil, filter the ferric oxide, etc., on an ashless filter, dry, ignite, and weigh, as described above. The manganese will be in the precipitate after ignition as manganoso-manganic oxide, and the amount calculated from the determination of manganese made in a separate portion of the ore must be subtracted from the weight of the above precipitate in calculating the amount of alumina.

The lime and magnesia are determined in the filtrate from the ferric oxide, etc., provided, of course, that the ore contains only minute amounts of nickel, copper, etc.

The same general method described above is applicable when the ore contains quite a large amount of titanic acid, so much, in fact, as to cause the cloudiness in the filtrate from the insoluble silicious matter, as noted on page 257. Whenever an acetate separation is necessary in an ore of this character, the precipitate must be filtered on an ashless filter, and this, as well as the filter containing any insoluble matter from the re-solution of the acetate precipitate, must be ignited and examined for titanic acid by treating the residue with hydrofluoric and sulphuric acids, heating to redness, fusing with sodium carbonate, dissolving in hydrochloric acid and water, and precipitating by ammonia. The precipitate so obtained is to be filtered, ignited, and the weight added to that of the ferric oxide, etc. Ilmenite even, when very finely ground in an agate mortar, is frequently capable of being almost entirely decomposed by hydrochloric acid, and when this is the case it is of advantage to use this method of analysis. It may be necessary, however, under certain circumstances to decompose the ore at the start by fusing with potassium bisulphate. To carry out this method, place 1 gramme of the ore, which has been ground as fine as possible in an agate mortar, in a large platimum crucible, add 10 grammes of pure potassium bisulphate, and heat the crucible, carefully covered, over a very low light until the bisulphate is melted. It is necessary to watch this operation most carefully, for the bisulphate has a strong tendency to boil over, and only unremitting attention on the part of the analyst will prevent the loss of the analysis. It is well at the start to stand by the crucible and raise the lid slightly at very short intervals to watch the condition and progress of the fusion. The lid should be held just over the crucible and in a horizontal position, otherwise the particles which have spirted on it from the mass in the crucible may run to the edge of the lid

and, when the latter is replaced, down the outside of the crucible. Raise the heat very gradually, keeping the mass just liquid and the temperature at the point at which slight fumes of sulphuric anhydride are given off when the lid is raised, until the bottom of the crucible is dull red. When the ore is completely decomposed, remove the light, take off the lid of the crucible, and incline the latter at such an angle that the fused mass may run together on one side of the crucible and as near the top as possible. Allow it to cool in this position; when cold it is easily detached from the crucible. Place the crucible and lid in a 600 c.c. beaker half full of cold water, and the fused mass in a little basket made of platinum gauze. Pour into the beaker enough strong aqueous solution of sulphurous acid to raise the liquid to the top of the basket, and allow the fusion to dissolve, which may require twelve hours. Wash with a jet of cold water, and remove the basket, the crucible, and the lid, stir the liquid, which should smell strongly of sulphurous acid, and allow the insoluble matter to settle. Filter on an ashless filter, wash well with cold water, dry, ignite, and weigh. Treat with hydrofluoric acid and 2 or 3 drops of sulphuric acid, evaporate to dryness, ignite, and weigh. The difference between the weights is silica. If any appreciable residue remains in the crucible, fuse with a little sodium carbonate, treat with sulphuric acid, and add to the main filtrate. To the main filtrate, which should be quite colorless and smell strongly of sulphurous acid, add a clear filtered solution of 20 grammes of sodium acetate and one-sixth of its volume of acetic acid (1.04 sp. gr.), heat to boiling, and boil for a few minutes. Allow the precipitate to settle, filter on an ashless filter, wash thoroughly with hot water containing one-sixth its volume of acetic acid, and finally with hot water, dry, ignite, and weigh as titanic acid. This precipitate, however, may not be quite pure, as small amounts of ferric oxide and alumina may be carried down with it. The best plan to pursue is to fuse with sodium carbonate, dissolve in water, filter, wash, dry, and fuse the insoluble sodium titanate, etc., with sodium carbonate, treat the cooled mass in the crucible with sulphuric acid, and precipitate and determine the titanic acid as directed above. The two filtrates from the treatment of the first precipitate of titanic acid may contain a little ferric oxide and alumina. To recover this, boil down the last filtrate until the greater part of the sulphurous acid has been driven off, add bromine-water to oxidize the iron, acidulate the aqueous filtrate from the sodium car-

bonate fusion with sulphuric acid, add it to this solution, boil the united solutions down in a platinum dish to a convenient volume, and add a slight excess of ammonia. Boil the solution until it smells faintly but decidedly of ammonia, filter, and wash slightly. Redissolve the precipitate in hydrochloric acid, and reprecipitate by ammonia, filter, wash, ignite, and weigh as ferric oxide and alumina to be added to the main precipitate. Boil the main filtrate and washings down in a large platinum dish after adding enough bromine-water to oxidize all the iron, add hydrochloric acid from time to time when necessary to keep the iron in solution, and, when reduced to a convenient bulk, nearly neutralize by ammonia, and boil. Filter, and wash the precipitate two or three times, redissolve and reprecipitate by ammonia, filter, wash, dry, ignite, and weigh as ferric oxide + alumina + phosphoric acid. Fuse this precipitate for a long time and at a high temperature with sodium carbonate, dissolve in water, wash by decantation, redissolve the residue of ferric oxide, etc., in hydrochloric acid, and determine the iron by titration. The alumina is obtained by difference, the phosphoric acid being determined in a separate portion. In the filtrate from the ferric oxide + alumina + phosphoric acid determine manganese, lime, and magnesia in the usual way.

DETERMINATION OF SILICA.

When silica alone is wanted in an ore a more rapid method is sometimes desirable. In this case dissolve 1 gramme of the ore in hydrochloric acid, evaporate to dryness, redissolve in dilute hydrochloric acid, filter on an ashless filter, wash, dry, ignite, and weigh the insoluble silicious matter. Treat this in the crucible with hydrofluoric acid and a few drops of sulphuric acid, evaporate to dryness, ignite, and weigh. It is evident now that if the insoluble silicious matter contains calcium, magnesium, potassium, or sodium, the loss of weight, which in the absence of these elements would represent the silica volatilized as silicon tetrafluoride, will be decreased by the amount of sulphuric acid which, uniting with these elements, remains as a part of the residue in the crucible. It is a simple operation, however, to fuse this residue with sodium carbonate, dissolve in water, acidulate with hydrochloric acid, heat to boiling, add solution of barium chloride and filter off, and weigh

the precipitated barium sulphate. This being accomplished, calculate the amount of sulphuric anhydride, and add its weight to the loss by volatilization. The result is the weight of silica. When the ore contains appreciable amounts of barium sulphate this method is not admissible.

Separation of Alumina from Ferric Oxide.

Besides the indirect method for determining alumina, it is sometimes necessary or convenient to make a direct separation. The method usually taken, the iron and alumina being in solution in hydrochloric acid, is as follows: Add to the solution about five times the weight of the oxides, of citric acid (tartaric acid may be used, but, as it is liable to contain alumina, citric acid is preferable) and excess of ammonia. If the solution remains clear, heat to boiling, and add a fresh solution of ammonium sulphide until all the iron is precipitated. If the solution does not remain clear on the addition of ammonia, acidulate with hydrochloric acid, add more citric acid, and then excess of ammonia. Allow the ferrous sulphide to settle, decant the clear liquid through a washed filter, throw the precipitate on the filter, and wash it well with water containing ammonium sulphide and ammonium chloride, changing the beaker into which the washings run before each addition of wash-water, and keeping the funnel well covered with a watch-glass. Unite the filtrate and washings, acidulate with hydrochloric acid, boil until the precipitated sulphur agglomerates, filter into a platinum dish, and evaporate to dryness. Heat carefully until the ammonium chloride is volatilized and there remains in the dish a mass of carbonaceous matter from the decomposition of the citric acid. The expulsion of the last traces of water from the ammonium chloride nearly always causes loss by spirting, but the difficulty may be entirely avoided by placing the dish in one of the holes of the air-bath overnight, after having lightly coated the upper edge of the dish with paraffine or grease to prevent the ammonium chloride from creeping over the top. This long heating expels the last traces of water without the least disturbance, and the dish may at once be placed over a Bunsen burner, and the mass in it decomposed without fear of loss. Transfer the carbonaceous matter to a crucible, wiping out the dish carefully with filter-paper, and placing these in the crucible also. Burn off the carbon in the crucible, fuse the residue with sodium carbonate and a little sodium nitrate, treat with water, transfer to a platinum dish, dissolve any adhering particles

in the crucible in hydrochloric acid, add this to the solution in the dish, with enough hydrochloric acid to acidulate it, heat to boiling after diluting, add a slight excess of ammonia, boil until the solution smells but faintly of ammonia, filter, wash thoroughly, ignite, and weigh as alumina. This precipitate will contain any phosphoric and titanic acids that may have been in the original solution. They may be separated by the methods given previously. It is liable to contain also a little iron, which is almost invariably held in solution by the ammonium sulphide.

Dissolve the precipitate of ferrous sulphide on the filter in dilute hot hydrochloric acid, allow the solution and washings to run into the beaker in which the precipitation was made, add a little nitric acid, evaporate to dryness, redissolve in as little dilute hydrochloric acid as possible, filter into a platinum dish, dilute, precipitate by ammonia, filter, wash, dry, ignite, and weigh as ferric oxide.

Rose * suggested the method based on the solubility of alumina in caustic potash or soda. When the iron and alumina are in solution, evaporate in a platinum dish until syrupy, add a strong solution of caustic soda or potash until the solution is strongly alkaline, and then add a large excess of the precipitant, and boil for ten or fifteen minutes; or, pour the nearly neutral solution of the chlorides into a boiling solution of caustic soda or potash in a platinum or silver dish, in a thin stream, stirring continually. Filter, wash with hot water, carefully acidulate the filtrate with hydrochloric acid, and precipitate the alumina by ammonia, filter, wash, dissolve in hydrochloric acid, evaporate to dryness to get rid of silica, redissolve, filter, and determine as usual. As the ferric oxide precipitated by caustic soda or potash always contains alkali, it must be dissolved in hydrochloric acid, precipitated by ammonia, filtered, and weighed in the usual manner.

Rose also suggested fusing the finely ground ignited oxides in a silver crucible with potassium or sodium hydrate; but this method, as well as the other, is open to the objection that it is almost impossible to get caustic soda or potash that does not contain alumina, and generally there is more in the reagent than in the ore.

Rivot suggested the following method. After weighing the ignited iron and aluminum oxides, grind them very fine, weigh them, and place in a

* Chimie Anal. Quant. (French ed.), page 148.

porcelain or platinum boat. Place the boat in a porcelain or platinum tube, and heat to redness in a current of hydrogen gas until no more water appears to come off. Replace the hydrogen by a stream of hydrochloric acid gas, reheat the tube, and continue the current as long as ferric chloride is given off. Replace the hydrogen by a stream of hydrochloric acid gas, reheat the tube, and continue the current as long as ferric chloride is given off. Remove the boat, and, if the residue is not white, repeat the operation. Weigh the remaining alumina, and calculate from the amount of the oxides used the total amount in the ore.

Rose modified this method by substituting a crucible and tube for the boat, etc. The apparatus as he used it is the same as that described for the determination of manganese as sulphide (page 107).

Wöhler suggested the method of separating iron and alumina by boiling the nearly neutral solution with an excess of sodium hyposulphite. The following modification of this method* appears to give excellent results, and has the advantage of doing away with a subsequent separation of phosphoric acid in those cases in which it has not been determined in another portion. The ferric oxide and alumina from 1 gramme of ore being in solution in hydrochloric acid, dilute to 400 or 500 c.c. with cold water, and add ammonia until the solution becomes dark red in color, but contains no precipitate. Now add 3.3 c.c. hydrochloric acid (1.2 sp. gr.) and 2 grammes sodium phosphate, dissolved in water and filtered; stir until the precipitate formed is dissolved and the solution becomes perfectly clear again. Add now 10 grammes of sodium hyposulphite, dissolved in water and filtered if necessary, and 15 c.c. of acetic acid (1.04 sp. gr.), heat to boiling, boil fifteen minutes, filter as rapidly as possible on an ashless filter, wash thoroughly with hot water, dry, ignite in a porcelain crucible, and weigh as aluminum phosphate, which, multiplied by .41845, gives the weight of alumina. It is necessary in burning off the precipitate to raise the heat very carefully until all the carbon has been burned off, as the aluminum phosphate may fuse and make it almost impossible to burn off the carbon.

The best method for separating alumina and ferric oxides is the phenylhydrazine method. Make an ether separation in the hydrochloric acid solution of the iron and alumina and proceed exactly as described on page 192.

* Communicated to the author by Mr. S. Peters in 1879.

DETERMINATION OF NICKEL, COBALT, ZINC, AND MANGANESE.

For the determination of these elements use 3 grammes of ore, dissolve in hydrochloric acid, add a little nitric acid or potassium chlorate to oxidize any ferrous oxide in the ore, evaporate to dryness, redissolve in hydrochloric acid, and evaporate a second time if necessary to get rid of all nitric acid. As noted on page 254, when the ore contains much organic matter, dissolve in hydrochloric acid (if there is much gelatinous silica, evaporate to dryness or the filtration will be much retarded), filter, add nitric acid or potassium chlorate, evaporate to dryness, redissolve in hydrochloric acid, and evaporate a second time if necessary, redissolve in 10 c.c. hydrochloric acid and 20 c.c. water, dilute, filter into a litre beaker, and proceed exactly as directed for the determination of manganese in iron and steel (page 103 *et seq.*) until the precipitate by hydrogen sulphide is obtained and filtered off. Determine the manganese, if desired, in the filtrate, as directed on page 105, and calculate to manganous oxide.

Dry and ignite the precipitated sulphides of nickel, cobalt, zinc, copper, lead, etc., in a porcelain crucible, transfer to a small beaker, and dissolve in hydrochloric acid, with the addition of a drop or two of nitric acid. Evaporate to dryness, redissolve in from 10 to 20 drops of hydrochloric acid, dilute to 50 or 60 c.c., heat to boiling, and pass a current of hydrogen sulphide through the boiling solution. Filter off the precipitated sulphides of copper, lead, etc., and wash with water containing hydrogen sulphide. Evaporate the filtrate, which contains only nickel, cobalt, and zinc, to dryness. To the dry salts in the bottom of the beaker add 2 drops of strong hydrochloric acid, dilute to 150 c.c. with cold water, and pass hydrogen sulphide through the solution until it is thoroughly saturated with the gas. If a white precipitate forms, it is zinc sulphide. Allow to stand several hours, filter, wash with hydrogen sulphide water (the zinc sulphide has a tendency to pass through the filter, and consequently the beaker into which the filtrate is received must be changed before the precipitate is poured on the filter), dry, and ignite the precipitate. Heat it several times with ammonium carbonate to drive off any sulphuric acid that may have been formed by the ignition, cool, and weigh as zinc oxide. The precipitate is yellowish white while hot and greenish-white when cold. If it should carry down a little cobalt from the

solution, the ignited precipitate of zinc oxide is green when cold. Pass hydrogen sulphide through the filtrate from the zinc sulphide again, and, if no further precipitate appears, add a few drops of a solution of .5 gramme of sodium acetate in 10 c.c. water. If this occasions a white precipitate, filter it off, after standing, as in the first instance; but if the precipitate is black (as it is almost certain to be if the instructions given above are strictly followed), add the rest of the sodium acetate solution, heat the solution to boiling, while the passage of the hydrogen sulphide is continued, allow the precipitate to settle, filter, ignite, and treat it as directed for the separation and determination of nickel and cobalt (page 105 *et seq.*).

DETERMINATION OF COPPER, LEAD, ARSENIC, AND ANTIMONY.

Treat 10 grammes of the finely ground ore with 50 c.c. hydrochloric acid, add a little potassium chlorate from time to time, and increase the heat gradually until the ore is perfectly decomposed. Dilute, filter into an 800 c.c. beaker, deoxidize with ammonium bisulphite, as directed on page 77, drive off the excess of sulphurous acid, and pass hydrogen sulphide through the solution for fifteen or twenty minutes. Allow the solution to stand for some hours until the precipitate has settled completely and the solution smells but faintly of hydrogen sulphide. Filter on a thin felt on the Gooch crucible or small cone, wash with cold water, and suck dry. Transfer the felt and precipitate to a small beaker, using a little asbestos wad in the forceps to wipe off any adhering precipitate from the large beaker and the crucible or cone, and digest it with a few c.c. of a colorless solution of potassium sulphide. Dilute to about 100 c.c., filter on another felt, and wash with water containing a little potassium sulphide. The solution contains the arsenic and antimony sulphides dissolved in potassium sulphide, while the copper and lead sulphides remain on the felt. Return the felt with the precipitate to the beaker from which they were filtered, and digest with hydrochloric acid, with the addition of nitric acid, until all the black sulphides are dissolved, dilute with a little hot water, and filter. Evaporate the filtrate, after adding a few drops of sulphuric acid, until fumes of sulphuric anhydride are evolved, allow to cool, dilute with 25 c.c. cold water, add one-half its bulk of alcohol,

allow to settle, filter the precipitated lead sulphate on the Gooch crucible, wash with alcohol and water, heat carefully over a low light, and weigh. Treat the precipitate on the felt under a slight pressure with a strongly ammoniacal solution of ammonium citrate, to dissolve the lead sulphate, wash with hot water, and weigh. The difference between the two weights is lead sulphate, which, multiplied by .68293, gives the weight of lead, or, multiplied by .78875, gives the weight of lead sulphide.

Evaporate the filtrate from the lead sulphate until the alcohol is driven off and the solution reduced to a convenient bulk, and precipitate the copper on a small platinum cylinder by electrolysis. The weight of copper multiplied by 1.25204, gives the weight of cuprous sulphide.

Acidulate the filtrate of potassium sulphide containing arsenic and antimony in solution with hydrochloric acid, and allow to stand in a warm place until all the hydrogen sulphide has been driven off and the arsenic and antimony sulphides mixed with the excess of sulphur have settled completely. Filter on a thin felt, wash with warm water, then with alcohol, and finally with carbon disulphide, to dissolve the excess of sulphur. Transfer the felt and precipitate to a small beaker, add 5 c.c. hydrochloric acid and a few crystals of potassium chlorate. Digest at a low temperature for some time, adding occasionally a small crystal of potassium chlorate, finally heat a little, but not to a sufficiently high degree to fuse any little particles of separated sulphur, keeping the liquid always full of the products of decomposition of the potassium chlorate. When all the arsenic and antimony sulphides are dissolved, dilute with about 20 c.c. of warm water, and add a few small crystals of tartaric acid to keep the antimony in solution. Filter from the asbestos, using as little wash-water as possible in order to keep down the volume of the solution, add a slight excess of ammonia to the filtrate, and if it remains clear 5 c.c. of magnesia-mixture and one-third the volume from time to time to precipitate the ammonium-magnesium arsenate.

Allow to stand overnight, filter, and determine the arsenic as directed on page 195. If the acid solution above mentioned becomes cloudy upon the addition of ammonia, acidulate carefully with hydrochloric acid, and add a little more tartaric acid. Then proceed as above directed. The weight of arsenic calculated from the amount of magnesium pyroarsenate, multiplied by 1.373, gives the weight of ferrous arsenide.

Acidulate the filtrate from the ammonium-magnesium arsenate, which contains none of the washings, with hydrochloric acid, so that the solution is just acid to test-paper, dilute with hot water to about 250 c.c., and pass hydrogen sulphide into the solution, heating it gradually to boiling. Drive off the excess of hydrogen sulphide with a current of carbonic acid, filter on a felt in the Gooch crucible, wash with water, alcohol, and finally with carbon disulphide to dissolve any free sulphur, dry carefully, heat to a temperature slightly above 100° C., and weigh as antimony trisulphide. For the very small amounts of antimony that are found in iron ores this method is sufficiently exact. The weight of antimony trisulphide, multiplied by .71424, gives the weight of antimony.

DETERMINATION OF THE ALKALIES.

As a rule, the alkalies in iron ores are found exclusively in the insoluble silicious matter, and when the sum of the weights of the silica, alumina, etc., lime, and magnesia in the insoluble silicious matter falls much below the weight of the latter, it is always well to look for alkalies.

Dissolve 3 grammes of the ore in hydrochloric acid, evaporate to dryness, redissolve in 10 c.c. hydrochloric acid and 20 c.c. water, dilute, and filter into a platinum dish. Ignite the insoluble residue, treat it in the crucible with hydrofluoric acid and from 10 to 30 drops sulphuric acid, evaporate down until the sulphuric acid is driven off, dissolve in water with a little hydrochloric acid if necessary, transfer to a small platinum dish, dilute to 100 c.c., heat to boiling, and add excess of barium hydroxide. Boil for a few minutes, and filter from the alumina, etc., into another platinum dish. Evaporate the filtrate to dryness, treat the residue with a little water, heat to boiling and add ammonium carbonate to precipitate the barium, filter into another platinum dish, evaporate to dryness, and heat to dull redness. Dissolve in a few c.c. of water, and filter into a weighed crucible.

Evaporate very low, and, if nothing separates out, add a few drops of hydrochloric acid, evaporate to dryness, heat to very dull redness, cool, and weigh as potassium chloride + sodium chloride. To the residue in the crucible add a little water, in which the residue should dissolve perfectly, and a solution of platinic chloride. Evaporate down in the water-bath until the mass in the

crucible solidifies upon cooling, add a little water to dissolve the excess of platinic chloride, and then an equal volume of alcohol. Filter on a Gooch crucible, wash with alcohol until the filtrate runs through perfectly colorless, dry at 120° C., and weigh as potassium-platinic chloride. This weight, multiplied by .19376, gives the weight of potash. Then multiply the weight of potassium-platinic chloride by .30673, which gives the weight of potassium chloride. Subtract this from the weight of potassium chloride + sodium chloride previously obtained, and the difference is the weight of sodium chloride, which, multiplied by .53028, gives the weight of soda.

To the filtrate from the insoluble silicious matter add an excess of ammonia, rub a little grease or paraffine on the edge of the dish, and evaporate the mass to dryness. This will render the ferric oxide very compact and granular. Dilute with hot water, add a few drops of sulphuric acid, evaporate to dryness, and ignite to drive off all the ammonia salts. Then proceed exactly as directed for the determination of the alkalies in the insoluble silicious matter. The alkalies in the insoluble silicious matter may also be determined by J. Lawrence Smith's method of fusion with calcium carbonate and ammonium chloride, as directed farther on (page 292).

The ammonium chloride, which is so troublesome in alkali determinations, may be decomposed* very easily by evaporating the solution down very low, transferring to a tall beaker or flask, and heating with a large excess of nitric acid,—3 or 4 c.c. nitric acid to every gramme of ammonium chloride supposed to be present. The decomposition takes place at a temperature below the boiling-point of water, and when the action seems to be over, transfer to a porcelain dish, and evaporate to dryness after adding a few drops of sulphuric acid. Dissolve in water, filter into a platinum dish, and proceed with the analysis in the usual way.

DETERMINATION OF CARBONIC ACID.

Weigh 3 grammes of finely ground ore into the flask A (Fig. 93), and connect the apparatus in the manner shown in the sketch. L, L are tabulated bottles for forcing a current of air through the apparatus. The air is deprived of any carbonic acid which it may contain by passing through the

* J. L. Smith, Am. Jour. Sci. and Art, 1871, 3d Ser., i. (whole No. 101) 269.

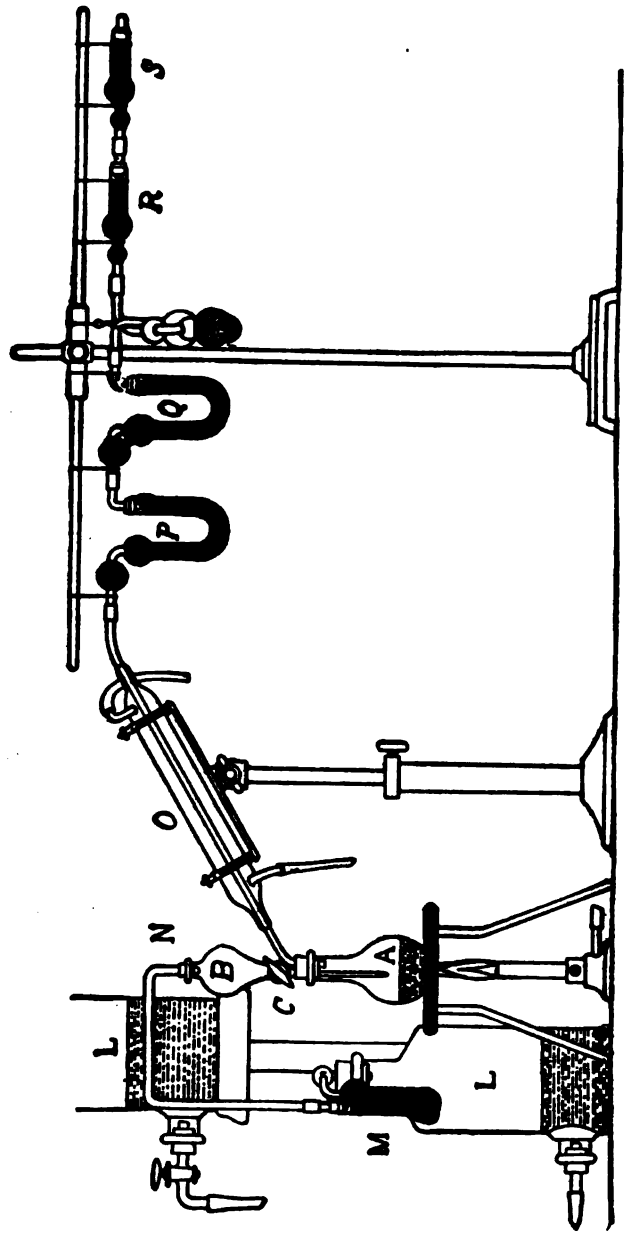


FIG. 93

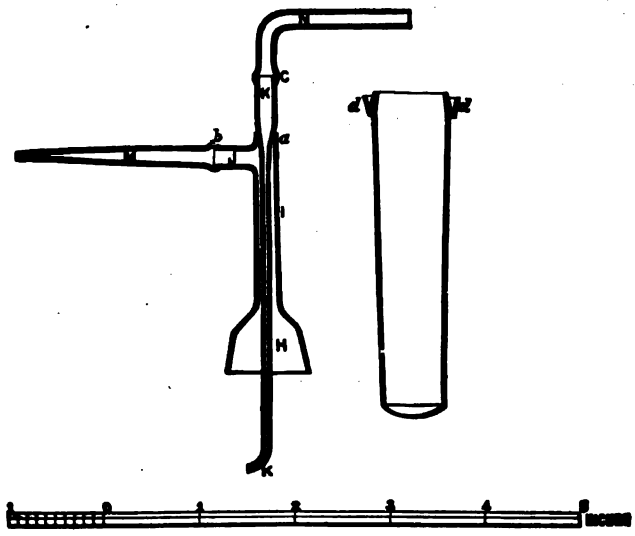
tube M, which is filled with caustic potash. M is connected with the bulb-tube B by the tube N, a piece of rubber tubing over the slightly tapering end making an air-tight connection with B. O is a condenser and serves to condense the steam and acid from the flask A. P contains anhydrous cupric sulphate, and Q contains calcium chloride. The potash-bulb and the drying-tube R form the absorption apparatus, and S is a safety-tube filled with calcium chloride to prevent R from absorbing moisture from the atmosphere. Weigh the absorption apparatus with the precautions mentioned on page 132, and connect the apparatus. Close the stopcock C, and draw a little air through the apparatus by means of a piece of rubber tubing attached to the end of S. Allow the tension of the air to draw the solution up into the rear limb of the potash-bulb, and if it remains there for a reasonable length of time the connections may be considered tight. Pour into the bulb B 10 c.c. hydrochloric acid diluted with about 65 c.c. water, connect the tube N, and by means of the stopcock. C allow the acid to flow slowly into the flask A. When the acid has all run in, by opening slightly the stop-cock in L, start a slow current of air through the apparatus. Warm the flask A, gradually increasing the heat until the solution boils, and continue the application of heat until a considerable amount of water has condensed in O. Allow it to cool while the current of air is continued, detach, and weigh the absorption apparatus. The increase of weight is the weight of carbonic acid.

DETERMINATION OF COMBINED WATER AND OF CARBON IN CARBONACEOUS MATTER.

The ores are very rare indeed in which the combined water can be determined accurately by simply heating them in a crucible and calling the loss by ignition "Water of Composition." Nor is the method of absorbing the moisture, driven off by heat, in a drying-tube much more reliable. The presence of pyrites, of organic matter, of graphite, and of manganese dioxide serves to complicate the problem. The water of composition may indeed be determined with great accuracy by heating the ore in a tube with lead chromate and potassium bichromate, exactly as described for the determination of carbon in iron and steel by direct combustion (page 142). The increase of weight of the U-tube which is attached to the end of the combustion-tube (and which in this case should be filled with granulated dried cupric sulphate)

is the weight of " Combined Water " in the amount of ore used. By attaching the absorption apparatus we likewise obtain the total carbonic acid in the ore, or that existing as carbonic acid in the carbonates, and that due to the oxidation of any carbon existing as carbonaceous or organic matter or as graphite. By subtracting from the weight of carbonic acid thus obtained the amount of carbonic acid existing as carbonate and determined by the method last given, and multiplying the difference by .27273, we get the weight of " carbon in carbonaceous matter." When it is necessary to make a large number of these determinations, the matter is very much simplified

FIG. 94

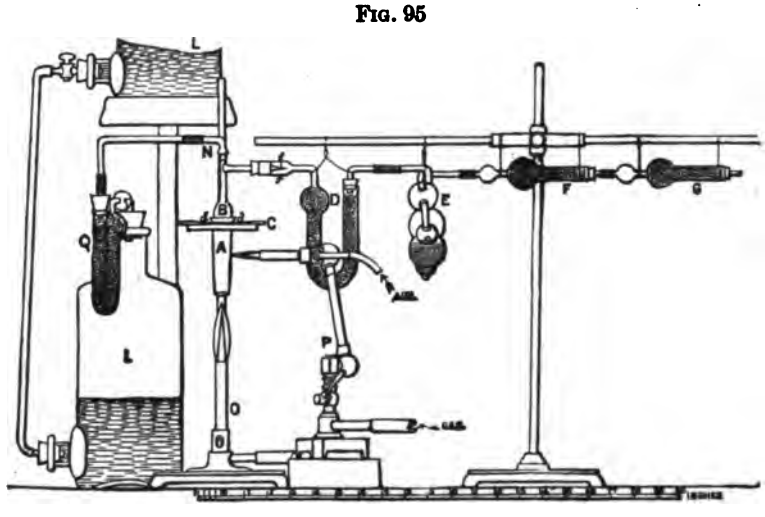


by using the apparatus shown in Figs. 94 and 95.* Fig. 94 shows the details of a form of tabulated platinum crucible suggested by Dr. Gooch, which consists of the crucible with a flange at *d* into which fits the cap. This cap consists of a conical cover, H, drawn up vertically into the tube I. The horizontal tube J is burned into I, and through the centre of I passes the small tube K, which, expanding at *a*, is burned into I at this point, sealing it securely. The glass tubes N and M are fused to K and J at C and *b* respectively. In analyzing ores containing much water or carbonic acid, use 1 gramme; for others, use 3 grammes. Weigh the finely ground ore, transfer it to a small agate mortar, and mix it thoroughly with from 7 to 10

* Tenth Census of the United States, Mining Industries, xv. 519.

grammes of previously fused potassium bichromate, transfer it to the crucible A (Fig. 95), and place it in an air-bath heated to 100° C. to drive off any hygroscopic moisture. When perfectly dry, attach the cap B to the crucible, and stand the latter in the triangle C. Close the end N with a piece of rubber tubing in the other end of which is fitted a piece of glass rod. Attach the weighed drying-tube D, filled with calcium chloride, to the horizontal tube from B, by means of a thoroughly dried velvet cork. Attach the absorption apparatus E and F and the safety-tube G. Fill the outside of the flange *d* with small pieces of fused sodium tungstate, and, with a blow-pipe flame, melt them, having previously immersed the lower end of A in a small beaker of ice-water. The expansion of the air in the crucible by the heat applied

FIG. 95



to melt the sodium tungstate will force some bubbles through the potash-bulb E, and the subsequent cooling of the air in A will cause the liquid in E to flow back into the rear bulb. If the difference of level thus produced be maintained for some minutes, the connections may be considered tight. Connect N with the bottles L, as shown in the sketch, and start a current of air through the apparatus. The air is purified from carbonic acid and miosture by passing through Q, which is filled with fused caustic potash. Now, by means of the blast-lamp P, heat the crucible just above the top of the mixture, and gradually carry the heat downward, increasing it at the same time. This will keep the mixture from frothing and choking the tube. Finally, heat the bottom of the crucible by the burner O, and continue the application of the

heat for ten minutes. During the whole of the operation the air passes through N and K into the crucible and out through J and M (Fig. 94) into D (Fig. 95), and so through the apparatus. The moisture from the ore should not be allowed to condense in the wide part of D at *f*, but should be driven forward into the calcium chloride by warming the tube at *f* with the flame of an alcohol lamp. Allow the apparatus to cool while the current of air is continued, then detach, and weigh the tube D and the absorption apparatus, and calculate the results as directed on page 282. When detached from the apparatus, the wide end of the tube D may be closed by a short cork, covered with tin-foil to prevent the absorption of moisture from the atmosphere. To clean the crucible, remove it from the stand, and, holding it in a piece of asbestos board in an inclined position, melt the sodium tungstate in the flange *d* with a blow-pipe flame and detach the cap. Dissolve out the bichromate by placing the crucible in a dish of hot water, clean out the ore, dissolve any adhering oxide in hydrochloric acid, wash the crucible and cap with hot water, dry them, and they will be ready for another determination.

DETERMINATION OF CHROMIUM.

The small amount of chromium which is found in some iron ores is generally converted into sodium chromate very readily by fusion with sodium carbonate and potassium nitrate. Fuse 1 or 2 grammes of the finely ground ore with ten times its weight of sodium carbonate and a little potassium nitrate. Treat the fused mass with water and wash it out into a small beaker. If the solution is colored by manganese, add a little alcohol, which will precipitate the manganese, leaving the solution, if chromium is present, slightly yellow. If the solution is colorless, it may be considered proof of the absence of chromium. Otherwise filter, wash the insoluble matter on the filter, dry it, grind it with ten times its weight of sodium carbonate and a little potassium nitrate, fuse, treat with water as before, filter, and add this filtrate to the other. Acidulate the combined filtrates with hydrochloric acid, evaporate to dryness to render the silica insoluble, and reduce the chromic acid to chromic oxide. Treat the mass with hydrochloric acid, dilute, filter, and precipitate the chromic oxide + alumina by ammonia. Boil for some minutes, filter, wash well with hot water, dry, and ignite the precipitate. Fuse

with as little sodium carbonate and potassium nitrate as possible, treat with water, and wash the solution into a platinum dish. Evaporate the solution until it is very concentrated, adding from time to time crystals of ammonium nitrate to change all the carbonated and caustic alkali to nitrate. At each addition of ammonium nitrate the solution effervesces, and ammonium carbonate is given off. When the solution is nearly syrupy, the addition of ammonium nitrate no longer causes an effervescence, and the solution smells faintly of ammonia, add a few drops of ammonia, dilute, and filter. By this operation all the alumina, aluminum phosphate, manganese oxide, etc., are precipitated, and there remain in the solution only the alkalies and the alkaline chromate. To the filtrate add an excess of sulphurous acid in water, which instantly changes the color of the solution from yellow to green. Boil well, add an excess of ammonia, boil for a few minutes, filter on an ashless filter, wash well with hot water, dry, ignite, and weigh as chromic oxide.

Chrome iron ore is best decomposed by fusing .5 gramme of very finely ground ore with sodium peroxide as described in the analysis of ferro-chrome (page 231), and proceeding as there directed.

DETERMINATION OF TUNGSTEN.

Digest from 1 to 10 grammes of the ore in hydrochloric acid, adding nitric acid from time to time. When the ore appears to be perfectly decomposed, evaporate to dryness on the water-bath (a higher temperature is not admissible, as it may render the tungstic acid insoluble in ammonia), redissolve in hydrochloric acid, and evaporate again. Redissolve in hydrochloric acid, dilute, filter, wash with acidulated water, and finally with alcohol. Treat on the filter with ammonia, allowing the filtrate to run into a platinum dish, evaporate to small bulk, add excess of ammonia, filter, if necessary, into a platinum crucible, evaporate carefully to dryness, heat gently to drive off the ammonia, and ignite. Weigh as tungstic acid.

Tungsten ores are analyzed like ferro-tungsten, page 216.

DETERMINATION OF VANADIUM.

Treat 5 grammes of very finely ground ore with hydrochloric acid and proceed exactly as in the determination of vanadium in steel (page 198).

DETERMINATION OF SPECIFIC GRAVITY.

The specific gravity of iron ores is determined with much greater accuracy by employing the powdered material than by using lumps of the ore. The little flask shown in Fig. 96 was designed for this purpose by the late Mr. James Hogarth,* and its use avoids two difficulties experienced with the ordinary specific gravity bottle,—the expansion and overflow consequent upon transferring the flask at 60° F. to the higher temperature of the balance-case, and the necessity for waiting until the finely divided particles of the ore shall have settled before inserting the stopper. These difficulties were overcome by melting a capillary tubulus to the lower part of the neck of the flask, and by grinding in a stopper having a small bulb above the capillary, to allow for expansion. The operation of determining the specific gravity of an ore is conducted as follows: Transfer a weighed amount of the ore to the flask, add enough water to cover it, and heat almost to the boiling-point by placing the flask without the stopper in the water-bath. Place the flask under a bell-jar connected with an aspirator or air-pump, and expel all the air by allowing the water to boil for some time at a reduced pressure. Remove the flask from the bell-jar, fill it to the tubulus with cold water, insert the stopper, and cool the flask and its contents to about 60° F. By suction on the stopper draw water through the tubulus until it is slightly above the capillary of the stopper, at which point a mark is scratched. When the flask and its contents are exactly at 60° F., adjust the volume exactly to the mark on the capillary by touching a piece of blotting-paper to the end of the tubulus or by drawing in a little water if the level is below the mark. Dry the flask, allow it to acquire the temperature of the balance-case, and weigh. Now, if W is the weight of ore taken, W′ the weight of the flask, the ore and water at 60° F., and K the weight of the flask full of water to the mark at 60° F., then

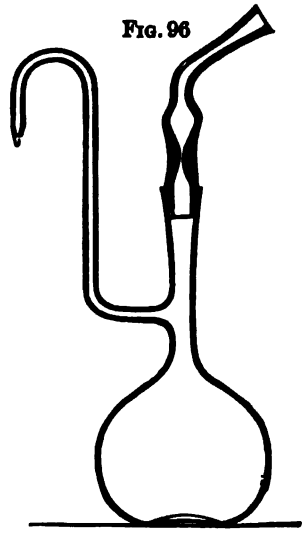


FIG. 96

$$\text{sp. gr.} = \frac{W}{W+K-W'}$$

To obtain K, fill flask with boiled water, and treat exactly as described above.

* Tenth Census of the United States, xv. 522.

METHODS FOR THE ANALYSIS
OF
LIMESTONE.

WEIGH 1 gramme of the powdered limestone, previously dried at 100° C., place it in a 250 c.c. beaker, cover with a watch-glass, and pour in 5 c.c. of hydrochloric acid diluted with 25 c.c. of water and a little bromine-water. Digest on the hot plate until all the action ceases, wash the watch-glass with a fine jet of water, and evaporate to dryness. Redissolve in 10 c.c. hydrochloric acid diluted with 50 c.c. water, filter on a small ashless filter, wash well with hot water, dry, ignite, and weigh as "Insoluble Silicious Matter." Heat the filtrate to boiling, add a slight excess of ammonia, boil for a few minutes, filter, wash once or twice. Dissolve the precipitate on the filter in a little dilute hydrochloric acid, allowing the solution to run into the beaker in which the precipitation was made, wash well with water, dilute, boil, and reprecipitate by ammonia. Filter on a small ashless filter, allow this filtrate to run into beaker containing the first one, wash well with hot water, dry, ignite, and weigh as alumina and ferric oxide. Heat the united filtrates to boiling, add enough ammonium oxalate to convert all the calcium and magnesium into oxalates.* Allow the precipitate of calcium oxalate to settle for fifteen or twenty minutes, decant the clear solution through an ashless filter, dissolve the precipitate in hydrochloric acid, dilute, add 10 c.c. of the ammonium oxalate solution, boil and precipitate by ammonia. Filter through the same paper, wash with hot water, dry, ignite for some time over a Bunsen burner, and finally for fifteen minutes at the highest temperature of a blast-lamp. Cool in a desiccator, weigh quickly, ignite again over the blast-lamp for five minutes, cool, and weigh again. If this weight is the same, or nearly the same, as the previous one, call the amount lime. If the second weight is much less than the first, ignite, and weigh again until the weight is constant. The weight of lime, multiplied by .178473, gives the weight of calcium carbonate. Add to the filtrate from the calcium oxalate 30 c.c. of a saturated solution of microcosmic salt (sodium-ammonium phosphate), acidulate with hydrochloric acid, and evaporate the solution to about 300 c.c. If during the evaporation

* 25 c.c. of the saturated solution is about the proper quantity.

any precipitate should separate out, redissolve it in hydrochloric acid. Cool the evaporated solution in ice-water, and add ammonia drop by drop, stirring the solution, but being careful to avoid rubbing the sides of the beaker with the rod, as the precipitate of ammonium-magnesium orthophosphate is liable to adhere with great tenacity to those points or lines where the rod has touched the sides or bottom of the beaker. Continue the addition of ammonia until the solution is decidedly alkaline, and then add an amount equal to one-fourth of the neutralized solution. After the precipitate has begun to form, stir vigorously several times, allow to stand over night, filter on an ashless filter, rub off with a "policeman" any of the precipitate that may adhere to the beaker, wash with a mixture of 1 part ammonia and 2 parts water, containing 100 grammes of ammonium nitrate to the litre, dry, ignite with great care, as directed on page 265, cool, and weigh as magnesium pyrophosphate, which, multiplied by .36207, gives the weight of magnesia, and, multiplied by .75719, gives the weight of magnesium carbonate.

Limestones, besides the ordinary constituents mentioned above, may contain small amounts of phosphoric acid, sulphur as sulphate or as pyrites, titanic acid, organic matter, combined water, alkalies, manganese, fluorine, and in rare instances nearly all the metals found in iron ores. For most of these the methods described in the analysis of iron ores may be employed. Very often the amounts of silica and alumina are required in calculating mixtures for the blast-furnace, and, as the matter insoluble in hydrochloric acid consists usually of alumina, lime, and magnesia silicates, it would be necessary in accurate work to decompose the 'Insoluble Silicious Matter" by fusion with sodium carbonate and to make a separate analysis of it, as described on page 264. It is, indeed, much better to make the analysis in this way than to add the filtrate from the silica to the main solution, for the calcium oxalate is sure to carry down some of the sodium salts with it and thus very materially complicate the analysis.

After weighing the alumina and ferric oxide from the "Insoluble Silicious Matter" and that from the portion soluble in dilute hydrochloric acid to determine the ferric oxide, fuse the two precipitates with a little sodium carbonate, dissolve in water, transfer to a beaker and acidulate with hydrochloric acid, add a few small crystals of citric acid to the clear solution, then excess of ammonia and ammonium sulphide. Allow the precipitate of ferrous sulphide to settle, filter, wash slightly, dissolve in hydrochloric acid, add a little bromine-water, boil the solution, precipitate by ammonia, filter, wash,

ignite, and weigh as ferric oxide. The weight of ferric oxide subtracted from the weight of the total alumina + ferric oxide gives, of course, the weight of alumina.

The lime and magnesia in the "Insoluble Silicious Matter" should not be calculated as carbonates, but should be considered as existing as lime and magnesia.

To determine phosphoric acid in limestones, treat 20 grammes with dilute hydrochloric acid, filter from the insoluble silicious matter, to the filtrate add a few drops of ferric chloride solution, then ammonia until the solution is alkaline to litmus-paper,* and acetic acid to decided acid reaction. Boil for a few minutes, filter, wash once with hot water, dissolve in hydrochloric acid on the filter, allowing the solution to run into the beaker in which the precipitation was made, add the solution from the treatment of the insoluble silicious matter mentioned below, dilute, and reprecipitate exactly as before with ammonia and acetic acid. Dissolve this precipitate on the filter in dilute hydrochloric acid, allowing the solution to run into a 250 c.c. beaker, wash the filter with hot water, evaporate the solution down almost to dryness, and precipitate the phosphoric acid as directed on page 76 or 99.

Ignite the insoluble silicious matter with hydrofluoric acid and a few drops of sulphuric acid, evaporate until fumes of sulphuric anhydride are given off, fuse with sodium carbonate, digest in water, filter, acidulate the solution with hydrochloric acid, and add it to the solution of the first precipitate in the soluble portion as mentioned above.

Instead of treating the insoluble silicious matter with hydrofluoric and sulphuric acids, it may be fused at once with sodium carbonate, the fused mass treated with water, filtered, the filtrate acidulated, evaporated to dryness, redissolved in water slightly acidulated with hydrochloric acid, filtered, and the filtrate added to the solution of the first precipitate by ammonia and acetic acid as above.

To determine sulphur in limestone, fuse 1 gramme with sodium carbonate and potassium nitrate exactly as in the determination of sulphur in iron ores (page 254 *et seq.*).

To determine sulphates, proceed as in the analysis of iron ores for these substances (page 255).

* If the precipitate is not decidedly red in color, acidulate with hydrochloric acid and add more ferric chloride solution.

METHODS FOR THE ANALYSIS
OF
CLAY.

CLAY is essentially silica, mixed with aluminum, calcium, magnesium, potassium, and sodium silicates. These silicates are hydrated, so that clay usually contains from 6 to 12 per cent. of water of composition. Besides these usual constituents, clay may contain ferric oxide, titanic acid, pyrites, organic matter, phosphoric acid, and occasionally some of the rarer elements, such as vanadium.

Clay being practically unacted on by hydrochloric acid, it is necessary to proceed as follows. Fuse 1 gramme of the finely ground clay, dried at 100° C., with 10 grammes of sodium carbonate and a very little sodium nitrate. Run the fused mass well up on the sides of the crucible, allow it to cool, and treat it with hot water until thoroughly disintegrated, transferring the liquid from time to time to a platinum dish. Treat the crucible with hydrochloric acid, add this to the liquid in the dish, acidulate with hydrochloric acid, and evaporate to dryness in the air-bath. Treat the mass with water and a little hydrochloric acid, evaporate again to dryness, and treat with 15 c.c. hydrochloric acid and 45 c.c. water. Allow it to stand in a warm place for fifteen or twenty minutes, add 50 c.c. water, and filter on an ashless filter. Wash thoroughly with hot water acidulated with a few drops of hydrochloric acid, dry, ignite, heat for three or four minutes over the blast-lamp, and weigh. Treat the precipitate with hydrofluoric acid and a few drops of sulphuric acid, evaporate to dryness, ignite, and weigh. The difference between the two weights is silica. If any appreciable residue remains in the crucible, treat it with a little hydrochloric acid, and wash it out into the filtrate from the silica. Transfer the filtrate from the silica to a large platinum dish, heat it to boiling, add a few drops of

* Determination of Aluminium as Oxide by Wm. Blum, Scientific Papers of the Bureau of Standards, No. 286.

methyl red * and an excess of ammonia, boil two minutes, filter on an ashless filter, and wash several times with hot water. Stand the filtrate and washings aside, and treat the precipitate on the filter with a mixture of 15 c.c. hydrochloric acid and 15 c.c. water (cold). Allow the solution to run into a small clean beaker, replace this by the platinum dish in which the precipitation was made, pour the solution on the filter again, and repeat this operation until the precipitate has completely dissolved. Rinse the beaker and wash the filter thoroughly with cold water, dry, and preserve it. Reprecipitate by ammonia, as above directed, filter on an ashless filter, wipe the dish with small pieces of filter-paper, add these to the precipitate, and wash thoroughly with hot water. Dry, ignite the precipitate and filter, and the filter from the first precipitation, heat for a few minutes over the blast-lamp, cool, and weigh as alumina and ferric oxide. Fuse the ignited precipitate with sodium carbonate, treat the fused mass with water, wash it into a small beaker, allow the residue to settle, decant off the clear, supernatant fluid, treat the residue with hydrochloric acid, and determine the iron volumetrically, or add citric acid and ammonia, and after precipitating the iron as sulphide, filter, wash, dissolve in hydrochloric acid, oxidize with bromine-water, and precipitate the ferric oxide by ammonia. Filter, wash, dry, ignite, and weigh as ferric oxide. Subtract the weight of ferric oxide from the alumina + ferric oxide found above, and the difference is alumina.

As the amounts of calcium and magnesium in clay are very small, the filtrate and washings from the second precipitation of alumina + ferric oxide may be rejected and the lime and magnesia determined in the first filtrate as directed on page 265.

To determine the alkalies in clay, treat 2 grammes of the finely ground material in a platinum dish with 4 c.c. of strong sulphuric acid and 40 or 50 c.c. of redistilled hydrofluoric acid. Stir it from time to time with a platinum wire or rod, heating carefully, until the clay is entirely decomposed and no more gritty substance can be felt under the rod. Evaporate to dryness, and heat until no more fumes of sulphuric anhydride are given off. The entire operation should be carried on under a hood with a good draft, as hydrofluoric acid is poisonous, and the evaporation may safely be conducted on the little arrangement shown in Fig. 8, page 17. Allow the dish to cool, add about 50 c.c. water and a little hydrochloric acid, and heat

until the mass is all dissolved. If any of the clay has escaped decomposition, filter into another platinum dish, wash the insoluble matter on the filter, dry, ignite, and decompose it in the crucible with hydrofluoric and sulphuric acids. Dissolve the mass in the crucible after evaporating off the hydrochloric and sulphuric acids, and add the solution to the main solution in the dish. Dilute this solution to 300 or 400 c.c. with hot water, heat to boiling, add an excess of barium hydrate, boil for a few minutes, and filter. Allow the precipitate to drain well on the filter, remove the filtrate, which should be in a platinum dish, to a light, and evaporate it down. Pierce the filter with a wire or rod, and wash the precipitate into the dish in which the precipitation was made with a jet of hot water. Dilute to 300 or 400 c.c., heat to boiling, filter, and wash several times with hot water. Add this filtrate to the first one, evaporate to dryness, and proceed exactly as directed for the determination of alkalies in the "Insoluble Silicious Matter" from iron ores (page 278).

Instead of decomposing the clay with hydrofluoric and sulphuric acids, the method given by J. Lawrence Smith may be used for determining alkalies. Place 1 gramme of the finely ground clay in a porcelain or agate mortar, add an equal weight of granular ammonium chloride,* and grind the two together to mix them. Add 8 grammes of calcium carbonate,† and grind the entire mass so as to obtain an intimate mixture of the whole. Transfer to a capacious platinum crucible, cover with a close-fitting lid, and heat carefully to decompose the ammonium chloride, which is accomplished in a few minutes. Heat gradually to redness, and keep the bottom of the crucible at a bright red for about an hour. Allow the crucible to cool, and if the mass is easily detached from the crucible, transfer it to a platinum dish and add about 80 c.c. of water. Wash the crucible and lid with boiling water, pouring washings into the dish. Heat the water in the dish to boiling, and, when the mass has completely slaked, filter into another platinum dish and wash the mass on the filter with hot water. If the semi-fused mass in the crucible is not easily detached, place the crucible on its side in the dish, add about 100 c.c. water, and heat until the mass disintegrates. Remove the crucible, rinse it, and filter as above directed. To the filtrate add about 1½ grammes of pure ammonium carbonate, evaporate on the

* See page 40. † See page 48.

water-bath, or very carefully over a light, until the volume of the solution is reduced to about 40 c.c., add a little more ammonium carbonate and a few drops of ammonia, and filter on a small filter. Evaporate the filtrate carefully after adding a few drops more of ammonium carbonate to make certain that all the lime has been precipitated. If any further precipitate appears, filter into a platinum crucible and evaporate to dryness. Heat carefully to dull redness to drive off any ammonium salts, and weigh the residue as potassium-sodium chloride. Separate the potash and soda as directed on page 278.

Determine the water of composition by igniting 1 gramme of the clay for twenty minutes at a bright red heat, when the loss of weight will represent the water. In the presence of much organic matter or pyrites the method given for the determination of water of composition in iron ores (page 281) may be used.

To determine titanic acid, treat 2 grammes of the finely ground clay in a large platinum crucible with hydrofluoric acid and 5 c.c. sulphuric acid. Evaporate off the hydrofluoric acid and heat carefully until the greater part of the sulphuric acid is volatilized. Allow the crucible to cool, add 10 grammes of sodium carbonate, and fuse for thirty minutes at the highest temperature obtainable by a Bunsen burner. Run the fused mass well up on the sides of the crucible, and allow it to cool. Treat the fused mass with water, transfer it to a beaker, and filter. Wash the insoluble matter slightly on the filter, dry, ignite, and fuse it again with sodium carbonate. Dissolve in water as before, and filter. By this method of treatment nearly all of the alumina will be dissolved and separated from the titanic acid. Fuse the insoluble matter left on the filter with sodium carbonate, and determine the titanic acid as directed on page 258.

When alkalies are determined, the precipitated alumina may be used for the determination of titanic acid. In this case dry the precipitate of alumina, etc., separate it from the filter, ignite the two filters, add the ash to the dried (not ignited) precipitate of alumina, etc., and fuse with sodium carbonate as above.

METHODS FOR THE ANALYSIS OF SLAGS.

BLAST-FURNACE slags contain silica, alumina, lime, magnesia, and alkalies always, generally also ferrous oxide, manganous oxide, and sulphur, and occasionally titanic acid, small amounts of phosphoric acid, and such metallic oxides as may exist in the ores, fluxes, or fuel used in the furnace. Sulphur, which is occasionally present in considerable amounts, is considered to exist in the slag as calcium sulphide.

The method used for the determination of the principal ingredients depends upon whether the slag is capable of being entirely or but partially decomposed by hydrochloric acid.

In the first case weigh 1 gramme of the finely ground slag, place it in a platinum or porcelain dish, add 20 c.c. of water, and shake the dish until the material is thoroughly disseminated through the water. Add gradually 30 c.c. hydrochloric acid, with constant stirring, and finally heat the dish carefully. The slag will dissolve completely to a clear liquid, but, after heating for a short time, will suddenly form a solid jelly. Evaporate carefully to dryness, treat with a few c.c. of dilute hydrochloric acid and a little bromine-water, evaporate again to dryness, and add 15 c.c. hydrochloric acid and 45 c.c. water. Allow to stand fifteen or twenty minutes in a warm place, add 50 c.c. water, filter on an ashless filter, wash thoroughly with hot water, dry, ignite, and weigh. Treat the material in the crucible with a little water, add 2 or 3 drops sulphuric acid and enough hydrofluoric acid to dissolve it. Evaporate to dryness, ignite, and weigh. The loss of weight is silica.

Any residue in the crucible after the volatilization of the silica is to be added to the alumina and ferric oxide. Heat the filtrate obtained above, diluted to 500 c.c., to boiling, add a slight excess of ammonia, boil for a few minutes, filter on an ashless filter, and wash two or three times with boiling water. Stand the filtrate aside, and pour on the precpitate in the

filter a mixture of 15 c.c. hydrochloric acid and 30 c.c. cold water, allowing the solution to run into the dish in which the precipitation was made. Alumina precipitated in this way seems generally to dissolve more readily in cold than in hot dilute hydrochloric acid, but it is often necessary to break up the precipitate on the filter with a rod, and pour the acid solution back on the filter several times after it has run through, or sometimes to pierce the filter with a rod or wire and wash the precipitate still undissolved into the dish. Wash the filter well with water, dry it, and keep it to ignite with the alumina, etc. Heat the filtrate and washings to boiling, reprecipitate by ammonia, filter on an ashless filter, clean off any adhering precipitate from the dish with filter-paper, add it to the precipitate on the filter, wash well with hot water, dry, ignite, after adding the filter on which the first precipitation was filtered, and weigh as alumina, etc. Add to this the weight of the residue from the treatment of the silica by sulphuric and hydrofluoric acids,* and the sum is the total alumina + ferric oxide + phosphoric acid + titanic acid.

Evaporate the two filtrates obtained above down to about 300 c.c., transfer to a 400 c.c. beaker, add a few drops of ammonia and enough ammonium sulphide to precipitate the manganese. Filter off and determine the manganese as directed on page 105 in the "Analysis of Iron Ores." To the filtrate from the manganese sulphide add a slight excess of hydrochloric acid, boil until all the hydrogen sulphide is driven off, filter from any precipitated sulphur, and determine the lime and magnesia as directed on page 287 *et seq.*, in the "Analysis of Limestone."

To determine the ferrous oxide, fuse the ignited precipitate of alumina, etc., obtained above, with 5 grammes of sodium carbonate, at a very high temperature, for at least thirty minutes. Allow the crucible to cool, treat the fused mass with water, transfer to a beaker, allow the insoluble matter to settle, decant the clear, supernatant liquid through a filter, and treat the residue with hydrochloric acid. Pour the solution through the filter to take up any iron that may have been suspended in the liquid decanted through it, and determine the iron volumetrically or by precipitation as sulphide in the solution to which citric acid and an excess of ammonia have been added, as on page 272. When the slag contains no appreciable amount

* This residue should be examined for lime.

of manganese, the precipitation by ammonium sulphide (page 295), may be omitted and the lime precipitated at once from the concentrated solution.

For the analysis of slags that are not entirely decomposed by hydrochloric acid, recourse must be had to fusion with sodium carbonate and a little sodium nitrate, exactly as described for the analysis of clay (page 290 *et seq.*). After filtering off the silica as directed (page 290), proceed with the analysis as described for slags decomposed by hydrochloric acid (page 294 *et seq.*). As, however, the calcium oxalate is very liable to carry down sodium salts with it, it is always well, after igniting the calcium oxalate, to dissolve it in dilute hydrochloric acid, transfer the solution to a platinum dish, dilute to 300 c.c. with hot water, add an excess of ammonia, and precipitate boiling by 30 c.c. of a saturated solution of ammonium oxalate. Filter, wash, ignite, and weigh in the usual manner.

For the determination of sulphur in slags, fuse 1 gramme with sodium carbonate and a little potassium nitrate, and proceed exactly as directed for the determination of sulphur in iron ores (page 254 *et seq.*). Calculate the total sulphur as calcium sulphide and the remainder of the calcium as lime.

For the determination of alkalies, titanic acid, etc., proceed as directed for the determination of these substances in clay.

Converter slags, open-hearth slags, refinery slag, tap cinder, mill cinder, etc., are analyzed by the methods described for the analysis of iron ores. In the case of slags obtained from the manufacture of steel by the basic process, which usually contain very large amounts of phosphoric acid, proceed as follows: Treat 1 gramme of the finely ground slag in a small beaker with 15 c.c. hydrochloric acid and a little nitric acid until it is decomposed. Evaporate to dryness, redissolve in 10 c.c. hydrochloric acid and 20 c.c. water, dilute, filter, and weigh the silica. To the filtrate diluted to 500 c.c. add a solution of ferric chloride and a slight excess of ammonia, if the precipitate is not decidedly red in color, acidulate carefully with hydrochloric acid, add more ferric chloride solution, and then a slight excess of ammonia. Add acetic acid to slight acid reaction, heat to boiling, filter and wash slightly with boiling water, stand the filtrate aside, and dissolve the precipitate on the filter in hydrochloric acid, allow the solution to run into the beaker in which the precipitation was made, wash the filter thor-

oughly with cold water, dilute the filtrate to about 400 c.c., add a slight excess of ammonia and then acetic acid, boil, and filter as before. Add this filtrate to the first, evaporate down, and determine the manganese, lime, and magnesia, as directed in the case of blast-furnace slags (page 294). Dissolve the precipitate on the filter in hydrochloric acid, dissolving any iron that may adhere to the beaker in a few drops of the same acid, pour it on the filter, and wash the beaker and filter well with water. Allow the solution and washings to run into a 600 c.c. beaker, and add about 10 grammes of citric acid and an excess of ammonia. To this solution, which should be cold, and should measure about 300 c.c., add, drop by drop, 50 c.c. of magnesia-mixture, stirring carefully, without touching the sides of the beaker with the rod. Add about one-third the volume of the solution of ammonia, allow the beaker to stand in ice-water for some time, stir vigorously several times, and after a few hours filter (preferably on a Gooch crucible), wash with ammonia-water of the usual strength, ignite carefully, and weigh as magnesium pyrophosphate. Any alumina in the slag will be in the filtrate from the ammonium-magnesium phosphate, and may be determined by the method on page 272. Determine the iron volumetrically in a separate portion, and calculate to ferrous oxide. Determine any other elements present by the methods under " Analysis of Iron Ores."

Phosphoric acid cannot well be determined in basic slags by fusion with sodium carbonate, as calcium phosphate is not readily decomposed by this method, and its employment may lead to error.

METHOD FOR THE ANALYSIS
OF
FIRE-SANDS.

As sand contains comparatively very small amounts of alumina, lime, and magnesia, and a very large amount of silica, it is best to proceed with the analysis as follows: Place 2 grammes of the finely ground sand in a large platinum crucible, moisten it with cold water, add 6 or 8 drops of sulphuric acid, and then gradually enough hydrofluoric acid to dissolve it. Evaporate to dryness (under a hood, of course), and heat to redness to drive off the sulphuric acid. Allow the crucible to cool, add a little sodium carbonate, and fuse. Dissolve the fusion, when cold, in water, add an excess of hydrochloric acid, evaporate to dryness, redissolve in hydrochloric acid and water, filter from silica, and determine the alumina, lime, and magnesia as usual. Ignite 1 gramme of the sand and determine the loss, which will be water and organic matter (if present).

It is well to note that in the presence of alumina it is almost impossible to drive off all the silica by treatment with hydrofluoric and sulphuric acids, and the small amount of silica remaining after this treatment must be separated as directed above.

Add together the percentages of water, alumina, lime, and magnesia, subtract the sum from 100, and call the remainder silica.

METHODS FOR THE ANALYSIS
OF
COAL AND COKE.

A PROXIMATE analysis affords a very rapid and comparatively simple way of classifying and valuing coal. From the nature of the material, the determinations cannot be absolute, but inferences may be drawn from the relative proportions of Moisture, Volatile Combustible Matter, and Ash. Therefore it is essential that the analysis should be performed in such a way as to obtain the most concordant results.

PROXIMATE ANALYSIS.*

Determination of Moisture.

"Dry one gramme of the coal in an open porcelain or platinum crucible at from 104° to 107° C. for one hour, best in a double-walled bath containing pure toluene.† Cool in a desiccator and weigh covered.

"With coals high in moisture, and in all cases where accuracy is desired, determinations must be made both with the coarsely ground and with the powdered coal. When, as will usually be the case, more moisture is found in the coarsely ground than in the powdered coal, a correction must be applied to all determinations made with the latter. Thus, if 1 per cent., more of moisture is found in the coarsely ground sample, a total of 1 per cent. must be subtracted from the quantities of the other constituents as determined with the powdered sample. Or, in the form of a rule: divide the difference in moisture by the per cent. of other constituents than moisture as found in the powdered coal by the quotient and subtract the resulting product from the amount of the given constituent.

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* From the Report of the Committee on Coal Analysis to the American Chemical Society, Journal of the American Chem. Soc., xxi, 1116. William A. Noyes, W. F. Hillebrand, and C. B. Dudley, committee.

† Victor Meyer, Ber. d. Chem. Ges., 17, 2999.

" Thus, suppose the results of an analysis give:

	Coarsely ground Coal	Powdered Coal
Moisture	12.07	10.39
Volatile combustible matter	....	34.25,

then the correction factor will be

$$\frac{12.07 - 10.39}{100 - 10.39} = \frac{1.68}{89.61} = 0.0187,$$

and the true per cent. of volatile combustible matter will be

$$34.25 - (34.25 \times 0.0187) = 33.61.$$

" It is possible that volatile combustible matter and ash may be determined with the coarsely ground coal without serious error, but we have not enough data at our command to warrant such a recommendation.

" The toluene bath is recommended for convenience, but any other bath at the proper temperature will answer equally well. In all cases recorded below the coals gained in weight, probably from oxidation, after one hour's heating, so that longer heating is not only unnecessary but undesirable. A higher temperature appears also to be undesirable."

Determination of Volatile Combustible Matter.

" Place 1 gramme of fresh, undried, powdered coal in a platinum crucible weighing 20 or 30 grammes and having a tightly fitting cover. Heat over the full flame of a Bunsen burner for seven minutes. The crucible should be supported on a platinum triangle with the bottom from 6 to 8 cm. above the top of the burner. The flame should be fully 20 cm. high when burning free, and the determination should be made in a place free from draughts. The upper surface of the cover should burn clear, but the under surface should remain covered with carbon. To find Volatile Combustible Matter, subtract the per cent. of moisture from the loss found here." (The weight of the material left in the crucible is " coke.")

Determination of Ash.

" Burn the portion of powdered coal used for the determination of moisture, at first over a very low flame, with the crucible open and inclined, till free from carbon. If properly treated, this sample can be burned much

more quickly than the dense carbon left from the determination of volatile matter. It is advisable to examine the ash for unburned carbon by moistening it with alcohol.

"When the sulphur in the coal is in the form of pyrites, that compound is converted almost entirely into ferric oxide in the determination of ash; and, since three atoms of oxygen replace four atoms of sulphur, the weight of the ash is less than the weight of the mineral matter in the coal by five-eighths of the weight of the sulphur. While the error from this source is sometimes considerable, the committee does not recommend such a correction for 'proximate' analyses. When analyses are to be used as a basis for calculating the heating effect of the coal a correction should be made."

Determination of Fixed Carbon.

"This is found by subtracting the per cent. of ash from the per cent. of coke as found above. Sulphur, which passes partly into the Volatile Combustible Matter and partly into the coke, is not considered in the calculation."

Determination of Sulphur.

Weigh 1 gramme of the finely ground coal or coke, and mix it thoroughly, by grinding in a large agate or porcelain mortar, with 10 grammes of dry sodium carbonate and 6 grammes of potassium nitrate. During the mixing it is well to have the mortar on a large sheet of white glazed paper, to catch any particles that may be thrown from it. Transfer the mixture to a large platinum crucible, clean the mortar by grinding a little sodium carbonate in it, transfer this and any particles that may be on the paper to the crucible, cover the latter with a lid, and place it on a triangle over an alcohol lamp. Heat the crucible very carefully, and raise the heat very slowly, cautiously removing the lid of the crucible from time to time to see that the fusion does not boil over. It is very necessary that an alcohol lamp be used for this fusion, as the sulphur in ordinary gas will certainly vitiate the result. When the mass in the crucible is in a tranquil state of fusion, run it up on the sides of the crucible, cool, treat with hot water, and wash out into a small clean beaker. Filter from the insoluble matter, acidulate the filtrate with hydrochloric acid, and evaporate to dryness. Redissolve in water with a few drops of hydrochloric acid, filter, dilute the filtrate to

about 500 c.c., heat to boiling, and add from 10 to 20 c.c. of a strong solution of barium chloride. Allow the precipitated barium sulphate to settle, decant the clear, supernatant fluid through a filter or a felt on a Gooch crucible, heat the precipitate with a solution of ammonium acetate, transfer it to the filter, wash well with hot water, dry, ignite, and weigh as barium sulphate, which, multiplied by .13734, gives the weight of sulphur. The time of the operation may often be very much shortened by adding an excess of ammonia to the acidulated filtrate of the aqueous solution of the fusion, and boiling the solution while passing a rapid current of carbonic acid gas through it. This precipitates the silica, alumina, etc., and, after filtering this off, acidulate by hydrochloric acid, and precipitate the barium sulphate as above directed.

A blank determination, using the same amount of sodium carbonate, potassium nitrate, and hydrochloric acid, should always be made with every new lot of reagents, and the amount of barium sulphate found subtracted from the amount of barium sulphate in every analysis before calculating the amount of sulphur in the coal or coke.

Determination of Sulphur.*

Eschka's Method.

"Eschka's method is recommended for general use. The following directions, which are given for the convenience of those using this report, are those of G. L. Heath † with slight modifications.

"Mix thoroughly 1 gramme of the finely powdered coal‡ with 1 gramme of magnesium oxide and ½ gramme of dry sodium carbonate in a thin platinum dish having a capacity of from 75 to 100 c.c. A crucible may be used, but a dish is preferred. The magnesium oxide should be light and porous, not a compact, heavy variety.

"The dish is heated on a triangle over an alcohol lamp, held in the hand at first. *Gas must not be used,* because of the sulphur it contains. The mixture is frequently stirred with a platinum wire and the heat raised very slowly, especially with soft coals. The flame is kept in motion and barely touching the dish, at first, till strong glowing has ceased, and is then in-

* From Report of Com. on Coal Analysis, *ante.*

† Journal American Chem. Soc., xx, 630.

‡ With coals high in moisture a correction may be necessary on account of the loss of water in powdering the coal. (See above under Moisture.)

creased gradually till, in fifteen minutes, the bottom of the dish is at a low red heat. When the carbon is burned, transfer the mass to a beaker and rinse the dish, using about 50 c.c. of water. Add 15 c.c. of saturated bromine-water and boil for five minutes. Allow to settle, decant through a filter, boil a second and third time with 30 c.c. of water, and wash till the filtrate gives only a slight opalescence with silver nitrate and nitric acid. The volume of the filtrate should be about 200 c.c. Add 1½ c.c. of concentrated hydrochloric acid or a corresponding amount of dilute acid (8 c.c. of an acid of 8 per cent.). Boil till the bromine is expelled, and add to the hot solution drop by drop, especially at first, and with constant stirring, 10 c.c. of a 10 per cent. solution of barium chloride. Digest on the water-bath or over a low flame, with occasional stirring till the precipitate settles clear quickly. Filter and wash, using either a Gooch crucible or a paper filter. The latter may be ignited moist in a platinum crucible, using a low flame till the carbon is burned.

"In the case of coals containing much pyrites or calcium sulphate, the residue of magnesium oxide should be dissolved in hydrochloric acid and the solution tested for sulphuric acid.

"If desirable, the burning of the coal with Eschka's mixture may be carried out in a muffle, from twenty to thirty minutes being required." *

By Fusion with Sodium Peroxide.†

Apparatus.

Crucible.—A soft steel or nickel crucible of about 40 c.c. capacity, the lid being perforated with a small hole for the introduction of the igniting wire.

Crucible Stand.—Any arrangement suitable for holding the crucible firmly in place and out of contact with the beaker during the peroxide combustion.

Method.

To the dry crucible add first 12 grammes of sodium peroxide and 0.5 gramme of powdered potassium chlorate, then exactly 0.7 gramme of coke (80 mesh) and mix thoroughly by means of a small spatula. Place the

* Rothe, Stahl und Eisen, xii. 31 (1894).
† Transaction American Foundrymen's Association, vol. xxv, page 706.

covered crucible on its stand in a 20-ounce beaker containing enough water to immerse the lower half of the crucible.

Ignite the crucible contents by thrusting in, for a moment, a red hot wire through the lid hole. Wait two minutes or longer for the mass to cool somewhat, remove the stand and tip over the crucible on its side in the water. After the fusion dissolves, rinse and remove the crucible.

Acidify the solution with hydrochloric acid, then add ammonia in slight excess, filter and wash. To the filtrate add a drop of methyl orange, then hydrochloric acid from a graduated pipette or burette until 0.5 c.c. in excess. Bring to boiling, add drop wise about 10 c.c. of barium chloride solution, and allow it to stand in a warm place for not less than two hours, filter, wash until the silver nitrate test shows no chlorides, ignite and weigh as $BaSO_4$.

$$\text{Grammes } BaSO_4 \times 19.6 = \text{per cent. sulphur.}$$

In reporting the results of a coal analysis the sulphur should always be reported as a separate matter, and no attempt should be made to distribute it between the Volatile Combustible Matter, Fixed Carbon, and Ash. The reason for this is obvious when we consider the conditions in which sulphur exists in coal, and the difficulty which attends any attempt to determine the amount existing in any one condition.

Sulphur is known to exist in coal in three conditions,—as a metallic sulphide, such as pyrites, as calcium or barium sulphate, and as a sulphuretted hydrocarbon. In a proximate analysis of coal about one-half the sulphur in any pyrites present and all the sulphur existing as a sulphuretted hydrocarbon are probably driven off with the Volatile Combustible Matter. The rest of the sulphur from the pyrites is oxidized and driven off during the burning of the Fixed Carbon (iron sulphate being easily decomposed at a bright red heat) unless the sulphuric acid formed is taken up by an alkali or alkaline earth.

The nearest approach we can make to a determination of the conditions in which the sulphur exists in any coal is to make a determination of the total sulphur by fusion, and a determination of the sulphuric acid in the ash. By subtracting the sulphur found by the latter determination from the total sulphur the difference may be taken to represent the amount existing as sulphur (in the form of sulphide), and the amount found in the ash as

that existing as sulphuric anhydride (in the form of sulphate). These results will be correct if the coal contains no carbonates of the alkalies or alkaline earths.

Determination of Phosphoric Acid.

Burn off 10 grammes of the coal or coke in a crucible, or, as in anthracite coal or coke this is a very tedious operation, burn it off in a large platinum boat in a tube in a current of oxygen. A boat 4 inches (102 mm.) long, and wide enough to fit in a tube ¾ of an inch (19 mm.) in diameter, will hold 10 grammes very easily, and by its use this amount of coke or anthracite coal may be burned off in a current of oxygen in about one and a half hours. Treat the ash with hydrochloric acid to dissolve any calcium phosphate, filter, and wash well with water. Stand the filtrate aside, dry, ignite, and fuse the insoluble matter with sodium carbonate. Dissolve in water, filter from the insoluble matter, acidulate the filtrate with hydrochloric acid, and evaporate to dryness. Redissolve in water and a little hydrochloric acid, add this filtrate to the hydrochloric acid filtrate from the first treatment of the ash, add a little ferric chloride solution and a slight excess of ammonia. Acidulate with acetic acid, heat to boiling, boil for a few minutes, filter, and wash the precipitate once or twice with boiling water. Dissolve the precipitate in hydrochloric acid, evaporate nearly to dryness, add citric acid, magnesia-mixture, and ammonia, and precipitate as directed on page 80. Filter, ignite, and weigh the magnesium pyrophosphate as there directed. Or, after dissolving the acetate precipitate, as above, in hydrochloric acid, evaporate down, and precipitate the phosphoric acid by molybdate solution, as directed on page 92 *et seq.*

ULTIMATE ANALYSIS.*

"It seems to be unnecessary to give directions for the determinations of carbon, hydrogen, and nitrogen here. In determining carbon and hydrogen, lead chromate or some other means for retaining sulphur must, of course, be used. The amount of nitrogen is so small that the use of a copper spiral is not necessary."

* From Report of Com. on Coal Analysis, ante.

"The method to be used in calculating the oxygen of the coal presents, perhaps, the question of greatest difficulty. If we could be sure that all of the sulphur is present in the form of pyrites, and that this is converted into ferric oxide in the ash, the oxygen should be found by subtracting from 100 the sum of carbon, hydrogen, nitrogen, ash, and five-eighths of the sulphur. This is probably the safest rule which can be given for general use, and especially for coals high in sulphur. The operator should, however, satisfy himself as to whether the ash is practically free from sulphates, and, if possible, whether the sulphur is mainly in the form of pyrites. If necessary, the rule should be modified, in particular cases, accordingly."

Heating Effect.

"In the preliminary report the recommendation was made that the heating effect be given on the basis of the coal burned to vapor of water at 100° C. After some criticism from others and further consideration, we have concluded to recommend that results be given for the coal burned to liquid water at the ordinary temperature. The reasons for this recommendation are that this appears to be the common practice in this country, and because coals are burned to liquid water in the bomb calorimeter, which undoubtedly furnishes the best determinations of heating effect at present available. Engineers and others will, of course, understand that the heating effect, when stated in this manner, includes from 3½ to 4 per cent. of heat which can never be secured under the conditions of practical use.

"The most reliable formula for the calculation of the heating effect of a coal burned to liquid water is that of Dulong, which gives the calorific power in calories per kilogramme.

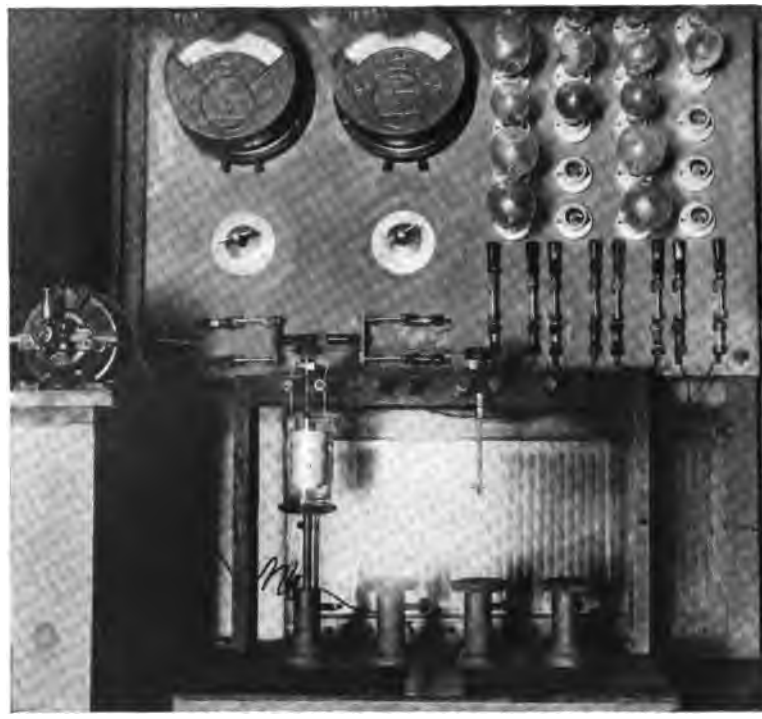
"Calorific power = 8080 C + 34,460 (H— ⅛ O) + 2250 S.

"For the calculation of the oxygen, see the paragraph above on ultimate analysis."

"The calorific power in British Thermal Units per pound may be found by multiplying that in calories per kilogramme by nine-fifths."

"The theoretical evaporative effect is to be calculated by dividing the number of calories per kilogramme by 536, or the number of British Thermal Units per pound by 965, and subtracting from the result one-seventh more than the amount of water formed by burning one kilogramme of the coal. The addition of one-seventh is given because the liquid water, on the basis of which the heating effect is given, must be considered as changed from

FIG. 97



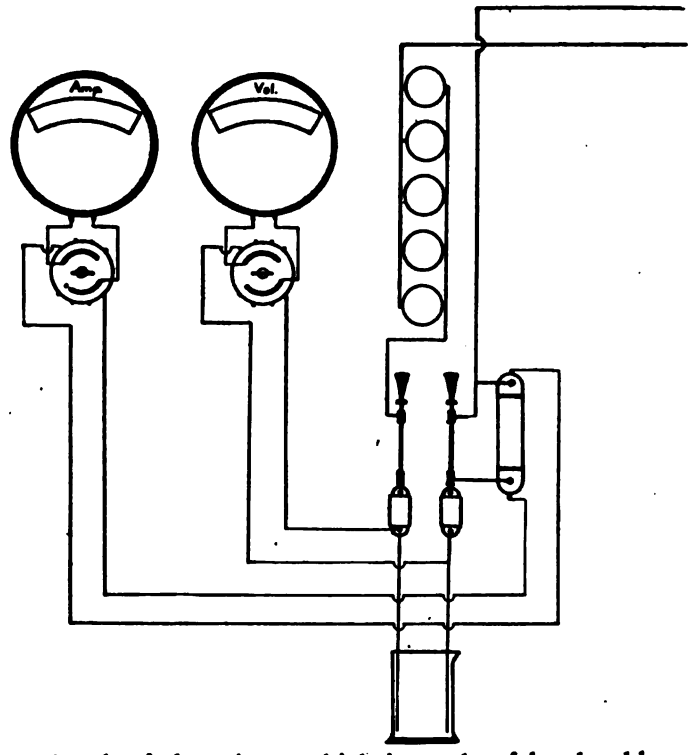
water at ordinary temperature to steam at 100° C. The amount to be subtracted may be taken as 0.55 for most bituminous coals. The result gives the theoretical number of kilogrammes, or pounds, of water converted into steam from, and at, 100° C. by one kilogramme, or pound, of coal."

"The rule given, tentatively, in our preliminary report for the calculation of heating effect, from the amount of combustible matter present in bituminous coals, has been found to be of limited application."

APPARATUS FOR THE DETERMINATION OF METALS BY ELECTROLYSIS.

Fig. 97 shows an arrangement for the determination of metals by electrolysis. The stirring arrangement is used instead of the rotating

FIG. 98



anode. A sketch of the stirrer which is made of hard rubber is shown in Fig. 99. The pointed end is received in a conical hole drilled in the

bottom of the precipitating jar to prevent vibration. The motor which actuates the stirrer receives its current through the simple nickel-iron wire rheostat shown under the switchboard. The details of the platinum electrodes and the clamps are shown in Figs. 100 and 101. One or both of the electrodes may be made of platinum wire gauze to increase the surface. Each circuit is independent and, as will be seen by the sketch

FIG. 99

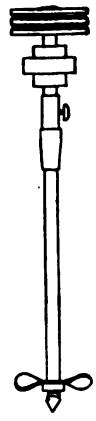


FIG. 100

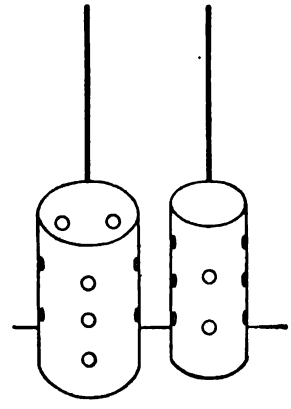


FIG. 101

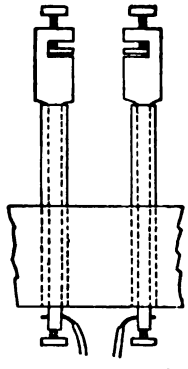
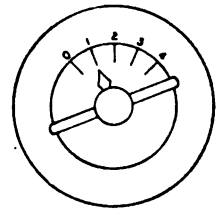


FIG. 102



of the wiring, Fig. 98, the amount of current is controlled by the character or number of the lamps or plugs screwed into the circuit. The current in each circuit may be read on the ammeter and voltmeter by the switches (the details shown in Fig. 102). The plan of wiring shows the shunt through which the current runs to the ammeter when the switch is pulled out.

The current from storage batteries is the best for electrolysis, although the ordinary direct current may be used. Where the alternating current alone is available, the best way of using it is to have an alternating motor in the current geared to a direct current generator. This current may be run through a storage battery of the number of cells required or it may be used directly.

TABLE I

ATOMIC WEIGHTS, 1917

Name	Symbol	At. Wt.	Name	Symbol	At. Wt
Aluminum	Al	27.1	Mercury	Hg	200.6
Antimony	Sb	120.2	Molybdenum	Mo	96.0
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Nitrogen	N	14.01
Bismuth	Bi	208.0	Oxygen	O	16.00
Bromine	Br	79.92	Phosphorus	P	31.04
Calcium	Ca	40.07	Platinum	Pt	195.2
Carbon	C	12.005	Potassium	K	39.10
Chlorine	Cl	35.46	Silicon	Si	28.3
Chromium	Cr	52.0	Silver	Ag	107.88
Cobalt	Co	58.97	Sodium	Na	23.00
Copper	Cu	63.57	Sulphur	S	32.06
Hydrogen	H	1.008	Tin	Sn	118.7
Iodine	I	126.92	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Lead	Pb	207.20	Uranium	U	238.2
Magnesium	Mg	24.32	Vanadium	V	51.0
Manganese	Mn	54.93	Zinc	Zn	65.37

TABLE II

TABLE OF FACTORS

Found	Required	Factor	Log.
$AlPO_4$	Al	0.22188	9.3461114–10
	Al_2O_3	0.41845	9.6216480–10
Al_2O_3	Al	0.53033	9.7245484–10
Sb_2O_4	Sb	0.78975	9.8974899–10
Sb_2S_3	Sb	0.71424	9.8538462–10
$Mg_2(NH_4)_2\ As_2O_8+H_2O$	As	0.39384	9.5953224–10
$Mg_2As_2O_7$	As	0.48274	9.6837141–10
As_2S_3	As	0.60918	9.7847480–10
As	$FeAs_2$	1.37246	0.1375014
$BaSO_4$	S	0.13734	9.1378068–10
$BaSO_4$	SO_3	0.34297	9.5352589–10
	BaO	0.65703	9.8175837–10
CaO	$CaCO_3$	1.78473	0.2515733
CO_2	C	0.27273	9.4357329–10
Cr_2O_3	Cr	0.68420	9.8351897–10
$CoSO_4$	Co	0.38038	9.5802154–10
	CoO	0.48358	9.6844718–10
Co	CoO	1.27132	0.1042564
CoO	Co	0.78658	9.8957436–10
Cu	CuO	1.25169	0.0974974
	Cu_2S	1.25216	0.0976609
CuO	Cu	0.79892	9.9025028–10
Cu_2S	Cu	0.79862	9.9023391–10
Fe_2O_3	Fe	0.69940	9.8447249–10
Fe_2O_3	FeO	0.89980	9.9541453–10
Fe	Fe_3O_4	1.38204	0.1405218
	FeO	1.28663	0.1094209
$PbSO_4$	Pb	0.68324	9.8345747–10
	PbO	0.73600	9.8668791–10
PbO_2	Pb	0.86622	9.9376286–10
$Mg_2P_2O_7$	P	0.27874	9.4451925–10
	P_2O_5	0.63793	9.8047737–10
	MgO	0.36207	9.5587913–10
	$MgCO_3$	0.75719	9.8792014–10
Mn_3O_4	Mn	0.72027	9.8574939–10
	MnO	0.93007	9.9685142–10
$Mn_2P_2O_7$	Mn	0.38691	9.5876130–10
	MnO	0.49961	9.6986334–10
MnS	Mn	0.63145	9.8003403–10
	MnO	0.81538	9.9113607–10
MoS_2	Mo	0.63949	9.8058326–10
MoS_3	Mo	0.49953	9.6985630–10
MoO_3	Mo	0.66667	9.8239109–10
NiO	Ni	0.78575	9.8952858–10
Ni_3S	Ni	0.78544	9.8951114–10
K_2PtCl_6	KCl	0.30673	9.4867567–10
	K_2O	0.19376	9.2872717–10
KCl	K_2CO_3	0.92677	9.9669723–10
NaCl	Na_2O	0.53028	9.7245029–10
	Na_2CO_3	0.90660	9.9574171–10
SiO_2	Si	0.46932	9.6714691–10
S	FeS_2	1.87087	0.2720430
SnO_2	Sn	0.78766	9.8963374–10
TiO_2	Ti	0.60050	9.7785126–10
V_2O_5	V	0.56044	9.7485288–10
WO_3	W	0.79310	9.8993279–10
ZnO	Zn	0.80337	9.9049142–10

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